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Ph. D. Dissertation

by

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Agrobiology and Agrochemistry

XXIII Cycle

Sorption of Trace Elements by Biotic and Abiotic Soil Components and Their Composites

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Index

1. Introduction

The occurrence of trace elements in cationic [Cu, Pb, Cd, Zn, Cr(III), Ni, Co, Hg] and anionic form [As, Se, Cr(VI), Mo, B] in natural environments have received increasing attention in the last decades because of their critical biological effects on plants, animals and humans. In trace amounts, some of these elements, e.g. Cu, Zn, Co and Se, are essential to living organisms or human beings, but they become toxic when their concentrations in the environment and in the organisms are sufficiently high. Some other elements, such as Pb, Cd, Hg and As, are generally hazardous to living organisms and human beings even at very low ambient concentrations (Jackson, 1998). Therefore, environmental pollution by trace elements is of great concern since their toxicity, increasing discharge, non-degradation and continual accumulation in the food chain (Iskandar and Kikham, 2001).

1.1 The source and pollution of trace elements

1.1.1 The source of trace elements

The average concentrations of Cu, Pb, Cd, Zn, Cr, Ni, Co, Hg, As and Se in worldwide soils are 20, 10-150, 0.06, 10-300, 20-200, 40, 10-40, 0.03, 9.36 and 0.20 mg kg^{-1}, respectively (He et al., 2005; and references therein), but their content in specific soils differed significantly, depending on their sources. The occurrence of trace elements in natural environment derives from both natural process and anthropogenic activities. Some elements occurred originally in igneous rocks or sedimentary rocks which make up of the whole earth crust. According to He et al. (2005), the concentration of Cu in basaltic igneous and shale clays is usually in the range of 30-160 and 18-120 mg kg^{-1}, respectively, while that of Cr is in the range of 40-600 and 30-590 mg kg^{-1}, respectively. Some elements are present in many natural minerals, for examples, Cu is present in malachite [$Cu_2(OH)_2CO_3$], azurite [$Cu_3(OH)_2(CO_3)_2$], tenorite [CuO], cuprite [Cu_2O], covellite [CuS], chalcocite [Cu_2S], digenite [Cu_9S_5], chalcopyrite [CuFeS], bornite [Cu_3FeS_4], enargite [Cu_3AsS_4] and tetrjedrote [$Cu_{12}Sb_4S_{13}$] (He et al., 2005), Pb is present in cerrusite [$PbCO_3$] and hydrocerrusite [$Pb_2CO_3(OH)_2$] (Cao et al., 2003), Zn is present in smithsonite

[$ZnCO_3$], sphalerite [ZnS] and hemimorphite [$Zn_4(OH)_2Si_{13}\cdot H_2O$] (He et al., 2005). The dissolution of these mineral in the weather development of soils or their erosion in sediments releases the enclosed elements, increasing the content of elements in local site. Facchinelli et al. (2001) evidenced that the output of Cr, Co, and Ni in the soils in Piemonte (NW Italy) was associated with and controlled by parent rocks. Chen et al. (2005) identified that the levels of Ni and Zn in the surface soils of urban parks in Beijing (China) were controlled by parent materials in the soils. Compared to data obtained in 1990, the contents of Cr and Ni in agricultural soils in Yangzhong district (China) remained steady in 2005 since they are derived from the weathering of parent material and subsequent pedogenesis (Huang et al., 2007). Zhang et al. (2009) also found that the presence of Ni in the soils of Fuyang County (China) was mainly determined by natural factors.

Anthropogenic activity is another source that increases the content of trace elements in terrestrial and aquatic environments. The application of trace element contained fertilizers, farm manures, pesticides, herbicides and fungicides in agricultural production, the misdischarge of domestic and industrial wastewater, the emission from smeltery and refinery of iron, steel and base metal, incinerator, factory of electric generation and fertilizer production, as well as from automobiles that use trace element enriched gasoline, and the exploitation of mine are the most important anthropogenic sources of trace elements (He et al., 2005; Wei and Yang, 2010). Facchinelli et al. (2001) found that the contents of Cu and Zn in the observed soils were controlled by a long term anthropic activities connected with grape-growing. Chen et al. (2005) found that the amounts of Cu and Pb in the examined soils were derived mainly from anthropogenic activities particularly vehicle emissions. Al-Khashman and Shawabkeh (2006) also showed that anthropogenic sources such as cement industry, agricultural activities and traffic emissions seemed to be responsible Pb, Zn and Cd pollution in soils around a cement factory in southern Jordan. The contents of Cd and Hg in an agricultural soil in Yangzhong district (China) were found to be higher in 2005 than in 1990, due to the long term use of agro-chemicals, the concentration of As, Cu, Pb and Zn showed slight increase during this period, and

it was ascribed to the atmospheric deposition of material sourced from urban anthropogenic activity (Huang et al., 2007). Zhang et al. (2009) found that 15.76% of the studied area suffered pollution by Cu, Pb and Zn, and 46.14% of the investigated area suffered moderate or severe pollution by Cd. Their spatial analysis identified that limestone mining activities, paper mills, cement factory and metallurgic activities were the main sources of these elements in soils.

1.1.2 Soil pollution by trace elements in China and Italy

Environmental pollution by trace elements became more and more serious in recent years because of the above nnthropogenic activities. Geoaccumulation index (I_{geo}) introduced by Muller (1969) is generally applied in assessing contamination levels, and it is classified as: uncontaminated ($I_{geo} \leq 0$), uncontaminated to moderately contaminated ($0 < I_{geo} \leq 1$), moderately contaminated ($1 < I_{geo} \leq 2$), moderately to heavily contaminated ($2 < I_{geo} \leq 3$), heavily contaminated ($3 < I_{geo} \leq 4$), heavily to extremely contaminated ($4 < I_{geo} \leq 5$), extremely contaminated ($I_{geo} > 5$). Wei and Yang (2010) have summarized the contamination of heavy metals in urban soils and agricultural soils of some Chinese cities. The I_{geo} value for Pb and Zn in urban soils of Baoji was 6.48 and 2.87, respectively, and that for Cu and Ni in urban soils of Jinchuan was 3.70 and 3.12, respectively, and that for Cd in urban soils of Changsha was 3.60, indicating serious pollution of the urban soils in these cites by the corresponding heavy metals. Moreover, the mean I_{geo} value for Pb and Cd in urban soils of all typical Chinese cities were 3.54 and 2.39, respectively, suggesting significant contamination of Pb and Cd in urban soils of typical Chinese cities. On the other hand, the mean I_{geo} values also revealed that the contamination by Cd and Hg was widespread in Chinese agricultural soils while agricultural soils in China were slightly polluted by Cr, Cu, Pb, Zn, Ni and As (Wei and Yang, 2010; and reference therein). A case study by Manta et al. (2002) reported that the mean concentrations of Pb, Zn, Cu and Hg in urban soils of Palermo (Sicily, Italy) were 202, 138, 63 and 0.68 mg kg^{-1}, respectively, which were higher, in some case by different orders of size, than those of unpolluted soils in Sicily whose average values were 44, 122, 34 and

0.07 mg kg^{-1}, respectively. In a study on the distribution of heavy metals in urban soils of Naples (Italy) in 1999, Imperato et al. (2003) found that total soil Cu, Pb and Zn content ranged from 6.2-286, 4-3420, 30-2550 mg kg^{-1}, with mean values of 54, 184 and 180 mg kg^{-1}, respectively. The maximum concentration of Cu, Pb and Zn established for soils of public, residential and private areas by Italian Ministry of Environment is 120, 100 and 150 mg kg^{-1}, respectively (Gazzetta Ufficiale della Repubblica Italiana, 1999), approximately 15%, 76% and 53% of examined urban soils of Naples in 1999 exceeded the limitation of Cu, Pb and Zn, respectively, moreover, the content of Cu, Pb and Zn in the surface layer of examined soils in 1999 was significantly higher than that in 1974, the accumulation from garden fertilizing activities, traffic and industry inputs was proposed for the enhancement.

1.2 Sorption of trace elements in soil constitutes

In natural environment, trace elements may be sorbed by soil components or sediments, dissolved in aquatic solution and/or accumulated by live organisms such as crops, vegetables and fishes, and then may enter into the food chains. Therefore, the sorption of these heavy metals on soil components or sediments relate closely to their mobility and bioavailability, and play a vital role in relieving their threat to human beings and animals.

1.2.1 Sorption mechanisms of trace elements on soil components

Soil components responsible for the sorption of trace elements include phyllosilicates, crystalline and noncrystalline (Fe, Al, Mn) oxides, humic substances, microorganisms, carbonates and so on, but they differ greatly in their sorption capacities and binding enerfies of their sorption sites (Violante et al., 2008).

Inner-sphere and outer-sphere surface complexes are generally defined by observing the configuration geometry of the adsorbate at the surface of adsorbent. When at least one water molecule of the hydration sphere is retained upon adsorption, the surface complex is referred as outer-sphere. When the ion is bound directly to the adsorbent without the presence of the hydration sphere, an inner-sphere complex is

formed (Sparks, 2002). Specific sorption which processed by the formation of inner-sphere complex and nonspecific sorption that progressed through the formation of outer-sphere complex are generally suggested by the scientific literature as the mechanisms of trace elements sorption (Sparks, 2002). Chemical complexation and electrostatic interaction (ion exchange) is the nature of specific sorption and nonspecific sorption, respectively. Moreover, specific sorption is characterized by a higher selectivity and stronger binding (weaker reversibility), while nonspecific sorption is known for lower selectivity and greater reversibility (Bradl, 2004). Therefore, sensitivity of heavy metal sorption to ionic strength has been considered to be a good indication to distinguish specific sorption and nonspecific sorption (Small et al., 2001; Li et al., 2006).

1.2.1.1 Sorption mechanisms of trace elements on phyllosilicates

Phyllosilicates are very important components of soils and are important scavengers for trace elements in cationic form due to their high cation exchange capacity (CEC). Montmorillonite is a typical 2:1 phyllosilicate, which possesses both permanent and variable charges. Isomorphic substitution of bivalent atoms for Al^{3+} in the octahedral layer is the origin of permanent charges, while the hydrolysis of hydroxyl on the broken edges is the source of variable charges. Both edge sites with variable charge on external surface and planar sites with permanent charge on interlayer surface are the available candidates of montmorillonite for scavenging trace elements. However, the sorption on edge sites is pH-dependent and thought to be complexation reaction while that on planar sites is pH-independent and considered to be ion exchange reaction (Hyun et al., 2000; Morton et al., 2001; Undabeytia et al., 2002). Sorbed heavy metals on the edge sites and planar sites have been also identified by EXAFS as inner-sphere complexes and outer-sphere complexes, respectively (Strawn and Sparks, 1999b; Morton et al., 2001). Furthermore, the distribution of sorbed heavy metals on edge and planar sites was controlled by solution pH and the concentration of background electrolyte. Many researchers found that the sorption of heavy metals on montmorillonite was pH-independent at stronger

acidic pH and lower electrolyte concentration while was pH-dependent at weaker acidic pH and higher electrolyte concentration, suggesting the shift of heavy metal sorption from planar sites to edge sites with the increase of both pH and electrolyte concentration (Fig. 1) (Strawn and Sparks, 1999; Hyun et al., 2000; Morton et al., 2001; Undabeytia et al., 2002).

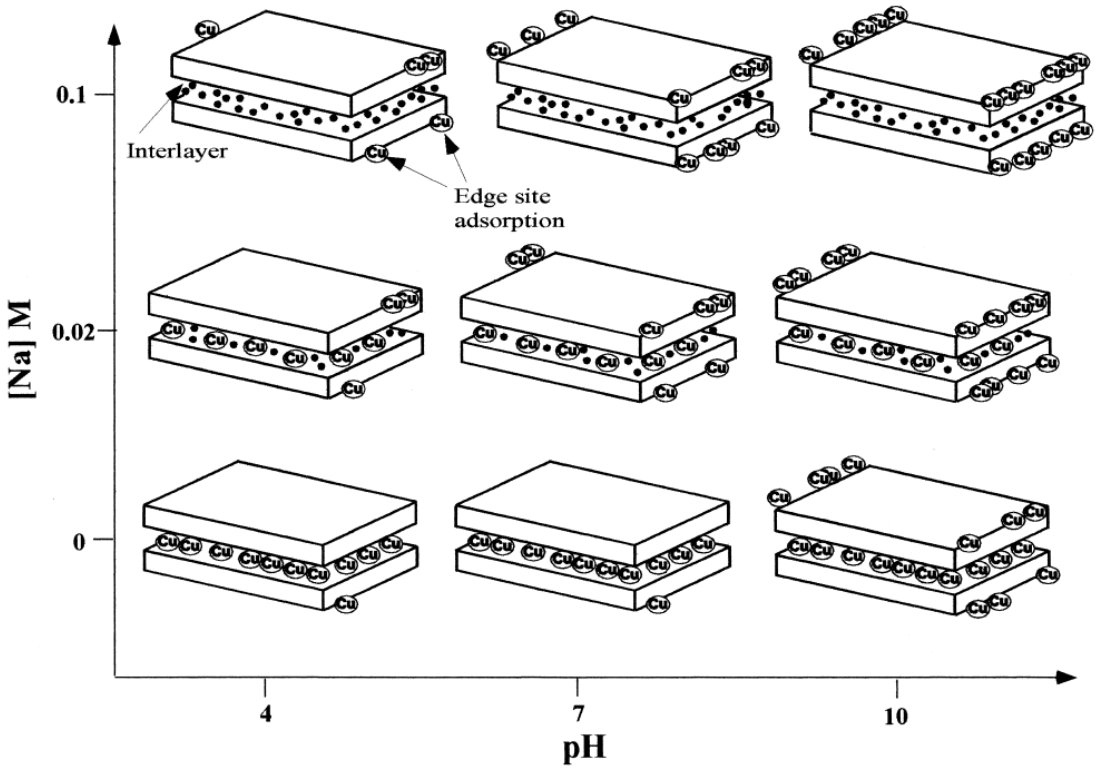

Fig.1. Schematic illustration of the effect of pH and Na concentration on the distribution of adsorbed copper on the permanent charge interlayer and edge sites of montmorillonite (Morton et al., 2001)

Kaolinite is a typical 1:1 phyllosilicate, whose structure consists of a tetrahedral silica sheet and an octahedral alumina sheet. Similar to montmorillonite, kaolinite possesses both permanent and variable charges. The formation of both outer-sphere and inner-sphere complexes of cationic trace elements on kaolinite have been found by macroscopic and spectroscopic investigations. Angove et al. (1997) revealed that Cd adsorption on kaolinite by two distinct processes: ion-exchange at the permanent charge sites on silanol faces and complexation with aluminol and silanol groups at crystal edges. The modelling of adsorption and potentiometric titration data also

suggested that the adsorption of Cu, Pb, Zn, Cd, Ni, Co and Mn on kaolinite involved both electrostatic attraction with permanent negatively charged sites on the silanol faces and inner-sphere complex with hydroxyl groups on the variable charged crystal edges (Ikhsan et al., 1999; Gu and Evans, 2008). EXAFS investigation evidenced that Cu was adsorbed on kaolinite as Cu^{2+} on ion exchangeable ≡X—H^{+} sites and as $(CuO_4H_n)^{n-6}$ and binuclear $(Cu_2O_6H_n)^{n-6}$ inner-sphere complexes on variable charge ≡AlOH sites by corner-sharing with two or three edge-sharing $Al(O, OH)_6$ polyhedra (Peacock and Sherman, 2005). The investigation on the sorption of Cd on kaolinite by EXAFS also confirmed the formation of outer-sphere complex at pH 7 and inner-sphere complex on edge sites at pH 9, moreover, the type of inner-sphere complex formed at pH 9 changed as a function of Cd loading (Vasconcelos et al., 2008).

1.2.1.2 Sorption mechanisms of trace elements on iron and aluminum oxides

Iron and aluminum oxides are among the most important scavengers for both cationic and anionic trace elements for their high surface area and great reactivity. Iron oxide comprises many types of minerals such as goethite, hematite, lepidocrocite, ferrihydrite and magnetite (Table 1). Specific sorption by the formation of inner-sphere complexes is suggested as primary mechanism for the retention of trace elements on iron oxides. However, the nature of inner-sphere complex is not generally identical. Lead ion was found to be hydrolyzed and adsorbed as mononuclear bidentate complex to the edge of FeO_6 oxtahedra on both goethite and hematite at pH 6-8 (Bargar et al., 1997b). Similarly, the sorption of Pb on ferrihydrite was dominated by mononuclear bidentate edge-sharing complex at pH ≥ 5.0 (Trivedi et al., 2003). However, at least two different surface complexes including mononuclear monodentate, mononuclear bidntate corner-sharing and mononuclear bidntate edge-sharing complex were found at lower pH, but the configuration of the sorption complex was independent of the adsorbate concentration at constant pH (Trivedi et al., 2003). The sorption of Cu on ferrihydrite formed similar complex (bidentate edge-sharing complex) to that of Pb at pH5 (Scheinost et al., 2001). While Peacock

and Sherman (2004) found that Cu was adsorbed as $(CuO_4H_n)^{n-6}$ and binuclear $(Cu_2O_6H_n)^{n-6}$ complex by corner-sharing with two or three edge-sharing $Fe(O, OH)_6$ polyhedra on goethite, hematite and lepidocrocite at pH2-7, the reaction of [2(≡FeOH) + Cu^{2+} + $2H_2O$ = $(≡FeOH)_2Cu(OH)_2^0$ + $2H^+$] and [3(≡FeOH) + $2Cu^{2+}$ + $3H_2O$ = $(≡Fe_3O(OH)_2)$ $Cu_2(OH)_3^0$ + $4H^+$] were proposed for the formation of bidntate corner-sharing mononuclear and tridentate corner-sharing binuclear surface complex (Fig.2), respectively. Moreover, no evidence was found for the formation of either monodentate corner-sharing or bidentate edge-sharing surface complex between $CuO_4H_n)^{n-6}$ and $Fe(O, OH)_6$ polyhedra (Peacock and Sherman, 2004).

Table 1 Major iron oxide and oxide hydroxides (Schwertmann and Cornell, 2000)

Oxyhydroxides	Oxides
Goethite (α-FeOOH)	Ferrihydrite ($Fe_5HO_8 \cdot 4H_2O$)
Akaganeite (β-FeOOH)	Hematite (α-Fe_2O_3)
Lepidocrocite (γ-FeOOH)	Maghemite (γ-Fe_2O_3)
Feroxyhyte (δ-FeOOH)	Magnetite (Fe_3O_4)

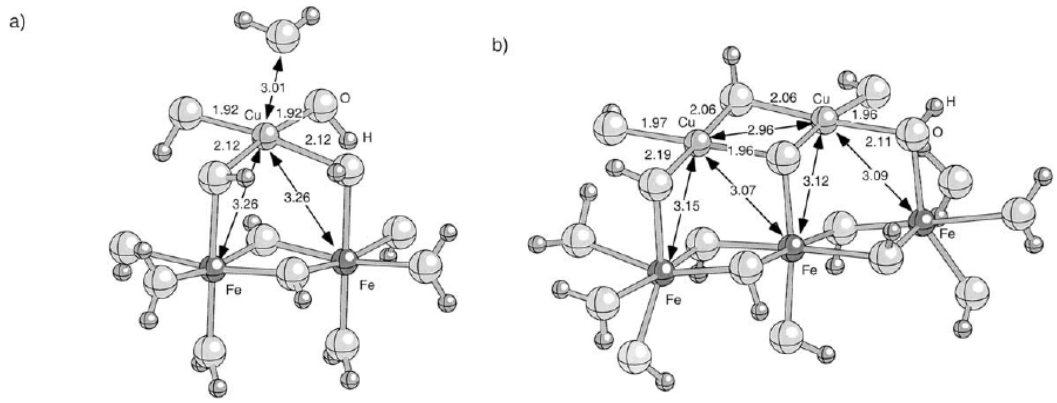

Fig.2. Bidentate corner-sharing mononuclear surface complex (a) and tridentate corner-sharing binuclear surface complex of Cu formed on goethite, hematite and lepidocrocite (Peacock and Sherman, 2004)

Arsenic is a typical anionic trace element, arsenate and arsenite are its prevalent forms in natural environments. The formation of various inner-sphere complexes has

been suggested as the primary mechanism for the sorption of arsenate on iron oxides (Fendorf et al. 1997; Goldberg and Johnston, 2001). However, both inner-sphere complexes and outer-sphere complexes have been found in the sorption of arsenite on iron oxides (Goldberg and Johnston, 2001; Ona-Nguema et al., 2005). The concrete species of inner-sphere complex formed by arsenate and arsenite is dependent on several factors such as surface coverage and the nature of iron oxide. It has been reported that arsenate formed three different surface complexes including monodentate, bidentate-binuclear and bidentate-mononuclear complexes on goethite (Fendorf et al. 1997). However, monodentate complex was favored at low surface coverage while bidentate complex was prevalent at high surface coverage, bidentate-binuclear complex appeared to be in the greatest proportion at the highest surface coverage (Fendorf et al. 1997). The EXAFS observation by Ona-Nguema et al. (2005) revealed that arsenite mainly formed bidentate mononuclear edge-sharing and bidentate binuclear corner-sharing complex on two-line ferrihydrite and hematite at high surface coverage, while a dominant amount of bidentate binuclear corner-sharing complex and a minor amount of monodentate mononuclear corner-sharing complex were formed on both goethite and lepidocrocite.

Aluminum oxides are another category of oxide that ubiquitous in natural environments. Sorption mechanism of trace elements on aluminum oxides is different from that on iron oxides in some extent. The formation of outer-sphere complex has also been found in some studies besides the formation of inner-sphere complex. Lead ion was found to be fully hydrolyzed and adsorbed preferentially as mononuclear bidentate complex to the edge of AlO_6 oxtahedra on Al_2O_3 at pH 6 and 7 (Bargar et al., 1997a). However, some other studies demonstrated that the sorption of solvated Pb ions on α-Al_2O_3 was processed by the formation of inner-sphere complex on α-$Al_2O_3(1\bar{1}02)$ and outer-sphere complex on α-$Al_2O_3(0001)$ (Bargar et al., 1996; Bargar et al., 1997c). Copper binding on γ-Al_2O_3 surface was interpreted as inner-sphere bidentate or monodentate complex on $Al(O, OH)_6$ octahedra (Cheah et al., 1998). An inner-sphere complex of Cu on boehmite (AlOOH) at low surface loading (< 0.2 μmol m^{-2}) at pH 6.5 was found by electron paramagnetic resonance

(EPR) and XAS, while a second population of $Cu(OH)_N$ $(H_2O)_X^{(2-N)+}$ outer-sphere complex was proposed at higher surface loading (Weesner and Bleam, 1997). The formation of inner-sphere complexes was found to be the mechanism of arsenate adsorption on gibbsite at pH 5.5 (Ladeira et al., 2000). Four different complexes including bidentate binuclear, bidentate mononuclear, monodentate mononuclear and monodentate binuclear complexes have been identified using density functional calculations, bidentate binuclear complexes was confirmed to be the most stable structure (Ladeira et al., 2000). The EXAFS observation by Arai et al. (2001) revealed that both arsenate and arsenite formed inner-sphere complexes with a bidentate binuclear configuration on γ-Al_2O_3. However, additional outer-sphere arsenite complexes were detected by XANES spectra, particularly by increasing pH (5.5-8.0) and decreasing ionic strength (Arai et al., 2001). Goldberg and Johnston (2001) found that the mechanism for the sorption of arsenate and arsenite on amorphous aluminum oxide was the formation of inner-sphere and outer-sphere complexes, respectively.

Layered double hydroxides (LDHs), which consist of positively charged layers and negatively charged interlayer anions, are known as “anionic clays” and postulated to be intermediate phases in the formation or dissolution of iron- or aluminum-(oxyhydro)oxides in natural environment (Roberts et al., 1999; Scheinost et al., 1999; Scheckel et al., 2000; Scheinost and Sparks, 2000; Schwertmann and Cornell, 2000; Yamaguchi et al., 2001; Livi et al., 2009). Many studies have demonstrated that these materials have a great capacity to retain anionic trace elements (Goh et al., 2008; and reference therein). On a Li/Al LDH-Cl, arsenate reacted not only with Al in the edges of $Al(OH)_3$ layers but also with Li located in the vacant octahedral sites within $Al(OH)_3$ layers (Liu et al., 2006). The sorption of arsenate on Li/Al LDH-Cl was six times higher than that on gibbsite (Liu et al., 2006).

1.2.1.3 Sorption mechanisms of trace elements on humic substances

Humic substances compose of humic, fulvic and humin fractions. They contain a variety of different organic functional groups such as carboxyls (-COOH), phenols (-OH), thiols (-SH) and amines ($-NH_2$) and show strong binding ability for trace

metals in cationic form (Senesi and Loffredo, 2008). In a acutely Zn-contaminated soil (about 2% dry weight) in Auby (Nord, France), Zn was found to be predominantly complexed with organic matter forming inner-sphere complexes (about 45%) and outer-sphere complexes (about 20%), precipitated with phosphate (about 10%) and sorbed on iron oxyhydroxides (about 10%), although Zn primary minerals (franklinite, sphalerite, and willemite) were present (about 15% of total Zn) in the bulk soil (Sarret et al., 2004). Similarly, in a Cu-contaminated agricultural soil in Hubbardsville, New York, most of Cu was found to be adsorbed on soil organic matter via bidentate inner-sphere coordination with carboxyl or amine ligands rather than on metal oxides, silicates, phosphates or carbonates (Strawn and Baker, 2008), suggesting the importance of humic substances in scavenging cationic trace elements. However, sorption behavior of trace elements on humic substances is very complex since the diversity and complexity of the structure and composition of humic substances. The understanding of the sorption mechanism and binding site of trace elements on humic substances become a hot topic for many years. Stevenson (1994) claimed that the formation of outer-sphere complexes (by electrostatic interaction) was the proper mechanism for the sorption of most divalent cations except Cu on humic substances. Some other researchers suggested that the formation of both outer-sphere complex and inner-sphere complexes (by chemical interaction) were the most siutable mechasms (Mcbride, 1978; Luster et al., 1996; Leenheer et al., 1998). The XAFS spectral fits of Ni solutions containing soil fulvic acid (standard Elliott soil fulvic acid, 2S102F) were found to be consistent with inner-sphere Ni coordination by one or more carboxylate groups, but spectra were noisy and outer-sphere modes of coordination were not ruled out (Strathmann and Myneni, 2004). Alvarez-Puebla et al. (2004) found that electrostatic retention rather than specific retention was the most important mechanism of Cu, Ni and Co retention on brown humic acids (BHAs) at very low cation concentrations, but this mechanism decreased progressively with the increase of cation concentrations. Moreover, during this process, BHAs modified its conformation slightly by decreasing surface area to coordinate with cations (Alvarez-Puebla et al., 2004). Many researchers emphasized or confirmed that the

formation of inner-sphere complexes was the most accurate mechanisms of trace elements sorption on humic substances (Xia et al., 1997a; 1997b; Korshin et al., 1998; Frenkel et al., 2000; Karlsson et al., 2005; 2006; Prado et al., 2006; Ghabbour et al., 2007; Manceau and Matynia, 2010).

Ligands in humic substances could coordinate with cationic trace elements through oxygen (O), nitrogen (N) and sulfur (S) donor atoms (Li, et al., 1998). Cadmium-113 NMR spectrometry observation showed that Cd was primarily coordinated by O donor atoms, probably in carboxyl groups, in a natural organic matter from Suwannee river near Farfo (Li et al., 1998). Infrared spectroscopy study also revealed that the interaction of Cu and Zn with an humic acid (HA) extracted from Brazilian peat soil occurred mainly at the carboxylic acid groups of HA (Prado et al., 2006). By considering the coordination of Cu in first, second and third coordination shell in EXAFS spectra, Karlsson et al. (2006) suggested that Cu was complexed by either one or two five-membered chelate rings involving possible combinations of amino, carboxyl or carbonyl functional groups in soil organic matter samples which collected from four different locations. Recently, Manceau and Matynia (2010) confirmed that Cu formed a five-membered Cu(malate)$_2$-like ring chelate at 100-300 ppm Cu concentration and a six-membered Cu (malonate)$_{1\text{-}2}$-like ring chelate at higher concentration at pH4.5 and 5.5 with four representative natural organic matter, moreover, the malate-type chelate showed stronger binding strength owed to an -OH for -H substitution on the α carbon. Nitrogen-containing functional groups similar or dissimilar to amino acids were also likely to be engaged in the complexation of Cu at low concentration in aquatic humic substances (Frenkel et al., 2000; Crouéet al., 2003). Karlsson et al. (2005) found that Cd complexed in soil organic matter was a mixture of a 4-coordination with S (thiols) and 4- and 6-coordinations with O/N ligands, but Cd-S associations on average were stronger than Cd-O/N associations, suggesting that reduced S ligands were involved in the complexation of Cd by natural organic matter.

1.2.1.4 Sorption mechanisms of trace elements on microorganism

Microorganisms, such as bacteria, are ubiquitous in natural environment, and their ability in scavenging cationic trace elements is also considerable (Ledin, 2000). Bacterial cell wall is known to have a number of functional groups such as carboxyl, phosphate, hydroxyl and amine (Ledin, 2000; Vijayaraghavan and Yun, 2008). Differently from humic substances, besides the formation of outer-sphere and inner-sphere complexes on cell wall, which are defined as passive uptake in biosorption, active uptake which transports the metal ions into the cell is another and a peculiar mechanism for scavenging trace elements by living bacteria (Ledin, 2000; Vijayaraghavan and Yun, 2008). In passive uptake, some studies found or inferred that nonspecific sorption was the primary mechanism (Shuttleworth and Unz, 1993; Ledin et al., 1997; Zouboulis et al., 2004; Özdemir et al., 2009), whereas other researchers demonstrated that specific sorption was the main mechanism of trace element retention (Boyanov et al., 2003; Burnett et al., 2006; Guiné et al., 2006). Pagnanelli et al. (2003) implied that specific sorption was the predominant mechanism at low metal concentration while ion exchange would take place when the specific sites were saturated with the increase of metal concentration. By monitoring the release of Mg^{2+}, Ca^{2+} and H^{+} during the adsorption of Cu^{2+}, Cd^{2+}, Zn^{2+} and Mn^{2+} on a fungal cell (*Saccharomyces cerevisiae*), Avery and Tobin (1993) confirmed that covalent bonding (H^{+} displacement) of the metal was greater at low metal concentrations, while weaker electrostatic interactions (Mg^{2+} plus Ca^{2+} displacement) became increasingly important at higher metal concentrations.

In specific sorption, carboxyl, phosphate and hydroxyl on bacterial cell wall are generally considered to be the most important candidates for binding cationic trace elements (Fein et al., 1997). The dissociation constant (p*K*a) of these functional groups and their thermodynamic stability constant (log*K*s) for metal binding have been sufficiently modeled by many researchers especially by Fein and his group (Fein et al., 1997; Daughney et al., 1998; Daughney and Fein, 1998; Fein et al., 2001; Yee and Fein, 2001; Ngwenya et al., 2003; Borrok et al., 2004; Borrok and Fein, 2005). As summarized in Table 2, the p*K*a values of carboxyl, phosphate, hydroxyl found on *Bacillus subtilis* and *Bacillus licheniformis* were 4.82 ± 0.14, 6.9 ± 0.5, 9.4 ± 0.6 and

5.2 ± 0.3, 7.5 ± 0.4, 10.2 ± 0.5, respectively. The thermodynamic stability constants (log*K*s) of carboxyl on *Bacillus subtilis* and *Bacillus licheniformis* for Cu, Pb, Cd binding were 4.4 ± 0.1, 4.2 ± 0.1, 3.4 ± 0.1 and 4.9 ± 0.4, 4.7 ± 0.3, 3.9 ± 0.5, respectively. However, Yee and Fein (2001) proposed that metal-bacteria adsorption was not dependent on the bacterial species as evidenced by the measurement of the thermodynamic stability constant for Cd binding on two Gram-negative and five Gram-positive laboratory cultivated bacteria strains. Borrok et al. (2004) confirmed that a wide range of bacteria strains cultured from natural environments exhibited similar adsorption behavior.

Table 2 Average surface characteristics and metal binding properties of *Bacillus subtilis*, *Bacillus licheniformis* and *Enterobacteriaceae* (Fein et al., 1997; Daughney et al., 1998; Ngwenya et al., 2003)

Bacterial strain	p*K*a			log*K*s	
	carboxyl	phosphate	hydroxyl	carboxyl	phosphate
Bacillus subtilis	4.82 ± 0.14	6.9 ± 0.5	9.4 ± 0.6	Cu: 4.4 ± 0.1 Pb: 4.2 ± 0.1 Cd: 3.4 ± 0.1	Cu: 6.0 ± 0.2 Pb: 5.6 ± 0.1 Cd: 5.4 ± 0.2
Bacillus licheniformis	5.2 ± 0.3	7.5 ± 0.4	10.2 ± 0.5	Cu: 4.9 ± 0.4 Pb: 4.7 ± 0.3 Cd: 3.9 ± 0.5	Cu: ---- Pb: 5.7 ± 0.7 Cd: 4.4 ± 0.7
Enterobacteriaceae	4.3 ± 0.2	6.9 ± 0.5	8.9 ± 0.5	Cu: 4.4 ± 0.2 Pb: 3.9 ± 0.8 Zn: 3.3 ± 0.1	Cu: ---- Pb: 5.0 ± 0.9 Zn: 5.1 ± 0.1

The importance of functional groups on bacterial cell wall in metal binding was affected by many factors such as bacterial strain, pH and bacteria to metal ratio. Electron spin resonance (ESR) study suggested that most of Cu on *Arthrobacter nicotianae* combined with amino acid residues in the cell surface proteins (Nakajima, 2002). The FTIR spectra indicated that the binding of Pb on *Bacillus cereus* involved

the carboxyl, hydroxyl and amino groups in the biomass (Pan et al., 2006). Phosphoester, carboxyl and unexpected sulfhydryl ligands were identified by combined titration, modeling and EXAFS observation as the binding sites of Zn on three bacteria (*Cupriavidus metallidurans* CH34, *Pseudomonas putida* ATCC12633 and *Escherichia coli* K12DH5R), but their proportion depended on Zn loading and bacterial strain (Guiné et al., 2006). Burnett et al. (2006) found that Cd adsorption on the cell wall of *Anoxybacillus flavithermus* occurred by the formation of a 1:1 complex with deprotonated carboxyl groups at high bacteria-to-Cd ratios, a second adsorption mechanism which may correspond to the formation of a Cd-phosphoryl, CdOH-carboxyl or CdOH-phosphoryl surface complex was observed at pH > 7 at lower bacteria-to-Cd ratios. The XAFS spectroscopy observation revealed that Cd bond predominantly to phosphoryl ligands on *Bacillus subtilis* below pH4.4, whereas the adsorption to carboxyl groups became increasingly important at higher pH, an additional phosphoryl site with smaller Cd-P distance than the one that was active at lower pH values was observed at pH7.8 (Boyanov et al., 2003).

1.2.2 Sorption kinetics of trace elements on soil components

Trace elements sorption on soil components can occur over time scales ranging from milliseconds to several months depending on the nature of sorbate-sorbent system (Sparks et al., 1999). Generally, the sorption of trace elements on clay minerals, (hydr)oxides and humic substances is characterized by a rapid reaction followed by a slow process (Sparks et al., 1999; Strawn and Sparks, 1999a). Half times for divalent Cu, Pb, Cd and Zn sorption on peat ranged from 5 to 15 seconds and were ascribed to film diffusion (Bunzl et al., 1976). Chemical reactions (adsorption) of Cu, Pb, Zn and Co on iron- or aluminium-oxides have been demonstrated to occur within millisecond time scales (Hachiya et al., 1984; Hayes and Leckie, 1986; Grossl and Sparks, 1994). Therefore, it is generally regarded that the rapid sorption of trace elements was controlled by film diffusion or chemical reaction (Scheidegger and Sparks, 1996a; Sparks et al., 1999). The slow step of metal sorption on many minerals occurred over time scales of days and longer (Bruemmer et al.,

1988; Barrow et al., 1989; Sparks et al., 1999; Fischer et al., 2007). Interparticle or intraparticle diffusion into pores and solids, sorption to the sites with low energy or reactivity and surface precipitation have been proposed to explain the slow process (Sparks et al., 1999). In addition, a fourth possibility, the formation of additional sorption sites due to the slow transformation of sorbent into a lower energy solid phase has been suggested by Strawn et al. (1998).

Soil and its mineral are porous and containing both macropores (> 2nm) and micropores (< 2nm), which can be between aggregates (inter-particle) or within an individual particle (intra-particle) (Sparks et al., 1999). Pore diffusion and solid diffusion thus were often proposed to account for the slow sorption of trace elements on soil components (Bruemmer et al., 1988; Papelis, 1995; Papelis et al., 1995; Axe and Anderson, 1997; Axe and Trivedi, 2002). By observing the sorption kinetics of Ni, Zn and Cd on goethite during a time period of 2 h to 42 d at pH6, Bruemmer et al. (1988) proposed that the adsorption of trace elements on goethite involved three steps: (1) adsorption of trace elements on external surfaces, (2) solid-state diffusion of trace elements from external to internal binding sites, (3) trace elements binding and fixation at positions inside the goethite particles, moreover, they suggested that the second step was the rate-limiting step.

The minerals may have binding site with different affinity. For instance, gibbsite has doubly coordinated hydroxyl group in the interior of the crystal and singly and doubly coordinated hydroxyl group at the edge faces, goethite is known to contain three different types of surface hydroxyl groups which are singly, doubly and triply coordinated to Fe atoms (Hiemstra et al., 1989). According to Hiemstra et al. (1989), the surface site density of these hydroxyl groups on the 100 plane of goethite was equal and was 3.3 sites per nm^2 for each type of group, however, only singly and doubly coordinated hydroxyl was found on 010 and 001 plane, the calculated site density of singly and doubly coordinated hydroxyl on both plane was also equal and was 7.1 sites per nm^2 on 010 plane and 8.6 sites per nm^2 on 001 plane, respectively, that was to say, singly, doubly and triply coordinated hydroxyl comprised 46%, 46% and 8% of total functional group sites on the surface of goethite. Moreover, Hiemstra

et al. (1989) found that doubly coordinated hydroxyl on goethite was predominately in the neutral form in the pH range from 4.0 to 6.0. Based on these findings, Grossl and Sparks (1994) speculated that the fast adsorption of Cu on goethite was ascribed to the association with doubly coordinated hydroxyl while the slow adsorption was due to the binding on singly and triply coordinated hydroxyl.

The formation of surface precipitation has also been suggested as a mechanism for the slow sorption of trace elements (Scheidegger and Sparks, 1996b; Scheidegger et al., 1997). However, the kinetics of precipitation formation is generally depends on reaction conditions (Sparks et al., 1999). Scheidegger et al. (1997) suggested that multinuclear Ni complexes appeared within a reaction time of minutes on pyrophyllite. In particular, XAFS analysis indicated that the formation of mixed Ni-Al precipitate on a soil clay fraction occurred within 15 min, 2h and 72h at pH 7.5, 6.8 and 6.0, respectively (Roberts et al., 1999).

Several models such as zeo-order, first-order, second-order, parabolic diffusion, power function and Elovich equation have been applied to describe the sorption kinetics of trace elements on various soil components (Table 3), but the suitability is depend on the concrete sorbate-sorbent system condition. For example, Raven et al. (1998) reported that the adsorption of arsenite and arsenate on ferrihydrite was described best by parabolic diffusion equation, while Pigna et al. (2006) found that the sorption of arsenate on four typical metal oxides [noncrystalline $Al(OH)_x$, gibbsite, ferrihydrite and goethite] followed Elovich equation best. First order equation was found to be the best to describe the adsorption of Pb on iron oxides formed under the influence of citrate (Liu and Huang, 2003), while the second order equation was found to be more appropriate in fitting the adsorption of selenite on hydroxyaluminum- and hydroxyaluminosilicate-montmorillonite complexes (Saha et al., 2004), the adsorption of Cd on aluminum precipitation products formed under the influence of tannate (Yu et al., 2006), the adsorption of Cd on Pb, Cu, and Cd on peat (Qin et al., 2006) and the adsorption of Cu on goethite and hematite nano-photocatalysts (Chen and Li, 2010).

Table 3 Linear forms of kinetic equations used (Violante et al., 2008)

Model	Linear equation
zeo-order	$C_t = a_1 - k_1 t$
first-order	$\ln C_t = a_2 - k_2 t$
second-order	$1/C_t = a_3 + k_3 t$
parabolic diffusion	$q_t = a_4 + Dt^{1/2}$
power function	$\ln q_t = \ln k + v \ln t$
Elovich equation	$q_t = (1/\beta) \ln \beta\alpha + (1/\beta) \ln t$

C_t is the amount of the element remaining in the soil (for desorption) or in solution (for sorption) at the end of the reaction time t; q_t is the amount of the element released (for desorption) or sorbed (for sorption) in time t; a_1, a_2 and a_3 are constants related to the amounts of the element in solution (for sorption) or in the soil (for desorption) at time 0; a_4 is the amount of element sorbed (for sorption) or released (for desorption) at time 0; k, k_1, k_2, k_3 and k_4 are constants; and D is an "apparent" diffusion coefficient.

1.2.3 Factors affecting the sorption of trace elements on soil components

The sorption of trace elements on soil components could be affected by many extrinsic factors such as solution pH, the presence of competitive ion, organic and inorganic ligands, ionic strength, temperature, redox conditions and so on. Among them, solution pH, competitive ion, organic and inorganic ligands are generally considered to be particularly important.

1.2.3.1 pH

Usually, the sorption of cationic trace element on soil components increases with the increase of pH while that of anionic trace element decreases with the enhancement of pH. The narrow pH range in which the sorption of heavy metal increases from 0 to 100% of the amount added is termed as "sorption edge", whereas the pH at which 50% of the total sorption occurred is called pH_{50}. It is well known that the pH edge for

Cu, Pb, Cd, Zn, Ni and Co on iron and aluminum oxides or natural polysaccharide moved to higher pH with the increase of metal concentration (Benjamin and Leckie, 1981a; Balistrieri and Murray, 1982; Tamura et al., 1983; Johnson, 1990; Reddad et al., 2002; Violante et al., 2008).

1.2.3.2 Competitive sorption

In contaminated environments, many different heavy metals and metalloids are usually present together. The competition among these trace elements for the sorption sites certainly has significant impacts on their sorption kinetics, capacity and affinity, and then affect their mobility and bioavailability, finally influence the toxicity to live organisms.

In single element system, sorption affinity of cationic trace elements on metal oxides or organic matters can be revealed by the pH_{50} value, generally, the lower the pH_{50}, the greater the affinity of trace element for the sorbent (Kinniburgh et al., 1976; Qin et al., 2006; Violante et al., 2008). As summarized in Table 4, among typical cationic trace elements, the affinity sequence of Pb > Cu > Zn > Ni > Cd > Co was found on freshly precipitated Fe gel and amorphous Fe oxyhydroxide (Kinniburgh et al., 1976; Benjamin and Leckie, 1981a), Cu > Pb > Zn > Ni > Co > Cd was found on freshly precipitated Al gel (Kinniburgh et al., 1976), and Pb > Cu > Zn > Co was found on mixed Fe-Al oxides which were aged for 7 days at 20^{o}C (Violante et al., 2003). The affinity of these trace elements on goethite has received much more attentions. The following sequence Hg > Cr > Cu > Pb > Zn > Co > Ni > Cd > Mn may be considered by combining the findings of many researches (Forbes et al., 1976; Mckenzie, 1980; Coughlin and Stone, 1995; Trivedi et al., 2001; Kosmulski and Mączka, 2004; Fischer et al., 2007). It is noteworthy that the affinity of Pb and Cu on amorphous Fe oxide and goethite or Al oxide is opposite, Pb shows greater affinity for amorphous Fe oxide and hematite than Cu while Cu shows higher sorption strength for goethite and Al oxide than Pb (Kinniburgh et al., 1976; Forbes et al., 1976; Mckenzie, 1980; Benjamin and Leckie, 1981a; Coughlin and Stone, 1995; Potter and Yong, 1999; Kosmulski and Mączka, 2004). The sequence of Pb > Cr > Cu,

Cd > Pb > Zn > Cu and Pb > Cu > Zn ≈ Ni > Cd was found on natural clinoptilolite, kaolinite and edge sites of Fithian illite, respectively (Inglezakis et al., 2003; Srivastava et al., 2005; Gu and Evans, 2007). For humic substances, although Pandey et al. (2000) reported that the stability constant (log *K*) of different heavy metal-humic acid complexes followed the order of Cu > Pb > Ni > Co > Cd > Zn > Mn, different affinity sequences of cationic trace elements for humic substances have been reported by other researchers (Table 5) (Beveridge and Pickering, 1980; Tipping and Hurley, 1992; Liu and Gonzalez, 2000; Chang et al., 2006; Qin et al., 2006), probably due to the diversity and complexity of the structure and composition of humic substances as pointed out before. Moreover, Kerndorff and Schnitzer (1980) found that pH was a potential factor in affecting the sorption sequence of trace elements on humic substance (Table 4). However, a sequence of Pb > Cu > Cd was supported by many literatures (Beveridge and Pickering, 1980; Liu and Gonzalez, 2000; Chang et al., 2006; Qin et al., 2006). On bacteria, the affinity sequence of Pb > Cu > Zn > Cd and Cu > Zn ≈ Ni was found on *Sphaerotilus natans* and *Thiothrix* Strain A1, respectively (Shuttleworth and Unz, 1993; Pagnanelli et al., 2003). Although the stability constants of Pb with carboxyl and phosphate on bacterial cell wall were lower that that of Cu (Table 2) (Fein et al., 1997; Daughney et al., 1998; Ngwenya et al., 2003), greater affinity of Pb than Cu on bacterial cell wall was found by Puranik and Paknikar (1999), Pagnanelli et al.(2003) and Tunali et al. (2006), probably due to the additional functional groups and sorption mechanisms involved.

Table 4 Sorption order of cationic trace elements at different pH on a humic acid extracted from a humic Gleysol at Ottawa (Kerndorff and Schnitzer, 1980)

pH	Sorption order
2.4	Hg > Pb > Cu > Ni > Cr = Zn = Cd = Co = Mn
3.7	Hg > Pb > Cu > Cr > Cd =Zn = Ni > Co = Mn
4.7	Hg = Pb = Cu = Cr > Cd > Ni = Zn > Co > Mn
5.8	Hg = Pb = Cr = Cu > Cd > Zn > Ni > Co > Mn

Table 5 Sorption affinity of cationic trace elements in single system on soil components

Sorbent	Affinity sequence	Reference
Freshly precipitated Fe gel	Pb > Cu > Zn > Ni > Cd > Co	Kinniburgh et al., 1976
Freshly precipitated Al gel	Cu > Pb > Zn > Ni > Co > Cd	Kinniburgh et al., 1976
Amorphous iron oxyhydroxide	Pb > Cu > Zn > Cd	Benjamin and Leckie, 1981a
Mixed Fe-Al oxide	Pb > Cu > Zn > Co	Violante et al., 2003
Hematite	Pb > Cu > Zn > Co	Mckenzie, 1980
Goethite	Cu > Pb > Zn > Co > Cd	Forbes et al., 1976
Goethite	Cu > Pb > Zn > Co > Ni > Mn	Mckenzie, 1980
Goethite	Cu > Pb > Ni ≈ Co > Mn	Coughlin and Stone, 1995
Goethite	Zn > Ni	Trivedi et al., 2001
Goethite	Cu > Pb > Zn > Co > Ni ≈ Cd	Kosmulski and Mączka, 2004
Goethite	Hg > Cr > Cu, Pb > Zn > Co, Ni > Cd > Mn	Fischer et al., 2007
Kaolinite	Cd > Pb > Zn > Cu	Srivastava et al., 2005
Natural clinoptilolite	Pb > Cr > Cu	Inglezakis et al., 2003
Edge sites of Fithian illite	Pb > Cu > Zn ≈ Ni > Cd	Gu and Evans, 2007
Humic acid	Pb > Cu > Cd > Zn	Beveridge and Pickering, 1980
Humic substances	Cu > Pb > Zn ≈ Ni > Co > Cd > Mn	Tipping and Hurley, 1992
Purified humic acid	Pb > Cu > Cd	Liu and Gonzalez, 2000
Humic substances	Pb > Cu > Cd > Zn	Chang et al., 2006
Peat	Pb > Cu > Cd	Qin et al., 2006
Sphaerotilus natans (Bacteria)	Pb > Cu > Zn > Cd	Pagnanelli et al., 2003
Thiothrix Strain A1 (Bacteria)	Cu > Zn ≈ Ni	Shuttleworth and Unz, 1993

The behaviors of trace elements in single sorbate system might be not enough to predict their sorption in multi system. For example, Srivastava et al. (2005) found that the pH_{50} values for the adsorption of Cu, Pb, Cd and Zn on kaolinite followed the

sequence of Cd > Pb > Zn > Cu in single adsorbate system while an order of Cd > Zn > Cu > Pb was observed in multi adsorbate system. A similar disagreement in pH_{50} values between single system (Zn > Cu > Pb > Cd) and multi system (Pb > Cu > Zn > Cd) of these four trace elements was observed on their adsorption by basic oxygen furnace slag (Xue et al., 2009). Therefore, studies on the competition in sorption among many trace elements are of paramount importance.

Competitive sorption among several heavy metals have been observed on many individual soil components. For instance, little or no competition among Cd, Cu, Pb and Zn in binary adsorbate system on an amorphous iron oxyhydroxide ($Fe_2O_3 \cdot H_2O$) was observed although an affinity sequence of Pb > Cu > Zn > Cd was revealed in single adsorbate system (Benjamin and Leckie, 1981a; 1981b), ascribing to the hypothesis that the surface of $Fe_2O_3 \cdot H_2O$ consisted of several distinct groups for metal binding. Palmqvist et al. (1999) revealed that the adsorption affinity of Cu, Pb and Zn on goethite followed the sequence of Cu > Pb > Zn in both single and ternary adsorbate system. Trivedi et al. (2001) and Xu et al. (2006) found that Zn was more effective than Ni in competitive adsorption on goethite. Capasso et al. (2003) reported that the competitive ability of Cr, Cu and Zn in the sorption on organic polymeric fraction of olive mill wastewater (polymerin) and its derivatives followed the order of Cr > Cu > Zn. Qin et al. (2006) found the order of Pb > Cu > Cd in their competitive adsorption on two Chinese peat. The sequence of Pb > Zn > Cu > Cd > Ni > Co was found in their simultaneous sorption on *Citrobacter* Strain MCM B-181 (bacteria) while greater competence of Cu than Zn in competitive binding was found on another bacterial strain (*Shewanella putrefaciens*) (Puranik and Paknikar, 1999; Claessens and Cappellen, 2007). Even though there was a disagreement in adsorption edge between single and multi system, Srivastava et al. (2005) also reported that a selectivity sequence of Cu ≥ Pb > Zn ≥ Cd was found in both single and multi elements systems in adsorption isotherm experiments. Covelo et al. (2007) conducted a special investigation to evaluate the preferential sorption of Cd, Cr, Cu, Ni, Pb and Zn by humified organic matter (HOM), Fe and Mn oxides, kaolinite, vermiculite and mica. The results revealed that kaolinite and mica preferentially sorbed and retained Cr,

vermiculite preferentially sorbed Cu and Zn, HOM, Fe and Mn oxides preferentially sorbed Pb (Covelo et al., 2007). Moreover, vermiculite and Mn oxide were found to retain the greatest proportions of sorbed metals (Covelo et al., 2007). More attentions about the competitive sorption among cationic trace elements were paid on various natural soils and these observations have been summarized in Table 6.

The competition among cationic trace elements could be affected by metal concentration, solution pH, temperature and, particularly, the nature of element and sorbent. No significant competition between Cu and Pb was observed at low metal concentration on hematite (Christl and Kretzschmar, 1999). Moreover, the competition between Pb and Cu in the adsorption on hematite was only observed in a narrow pH range from 4.5 to 6.3 (Christl and Kretzschmar, 1999). Heidmann et al. (2005) found that the sorption of Cu on kaolinite decreased in the presence of Pb at low pHs while no influence of Pb on the sorption of Cu was observed at higher pH. Liu et al. (2009) showed that the sorption of Cr was lower than that of Cu at 10 ^{o}C when equimolar amounts of the two elements were added as a mixture on a wine-processing waste sludge, however, the order was reversed after a reaction of about half an hour at 30 ^{o}C, and higher sorption of Cr over Cu was observed at 50 ^{o}C.

The intrinsic nature of element such as first hydrolysis constant, electronegativity, ionic radii and softness have also been proposed to explain the preference of trace element sorption in multi system (Gomes et al., 2001; Saha et al., 2002; Qin et al., 2006; Flogeac et al., 2007; Jalali and Moharrami, 2007; Usman, 2008; Vidal et al., 2009). For example, the consistency of selectivity sequence with the first hydrolysis constant of examined metals have been implied by Saha et al. (2002), Flogeac et al. (2007), Usman (2008) and Vidal et al. (2009).

The nature of the sorbent is another important factor that influences the selectivity of trace elements in competitive sorption. As mentioned above, Covelo et al. (2007) found that each soil component showed different preference to adsorb cationic trace elements. By comparing the competitive adsorption of cationic trace elements on the soil before and after the removal of organic matter or hydrous oxides, Fontes and Gomes (2003) found different selectivity sequence on Brazilian soils,

Agbenin and Olojo (2004) revealed that the binding sites in the amorphous hydrous oxides and organic matter of Alfisol in Nigeria were more selective for Cu than for Zn, Pérez-Novo et al. (2008) reported that Cu was adsorbed more than Zn in competitive adsorption on both untreated and treated soil but the removal of organic matter reduced the adsorption of Cu to a greater extent than Zn.

Table 6 Selectivity of various soils for cationic trace elements in multi system

Soil	The most common sequence	reference
Soil of Sacramento (USA)	pH4.5: Pb > Cu > Zn > Ni > Cd ≈ Cr pH6.5: Pb > Cu ≈ Zn > Cd > Ni > Cr	Gao et al., 1997
Brazilian soils	Cr > Pb > Cu > Cd > Zn > Ni; Pb > Cr > Cu > Cd > Ni > Zn;	Gomes et al., 2001
Dystryc Fluvisols, Haplic Luvisol, Gleyic Podzol	Cu > Zn	Mesquita et al., 2002
Brazilian soils	Cr ≈ Pb >> Cu >>> Ni > Cd ≈ Zn	Fontes and Gomes, 2003
Humic umbrisols of Pontevedra (Spain)	Pb > Cr > Cu > Cd ≈ Ni ≈ Zn	Covelo et al., 2004
Alfisol of Nigeria	Cu > Zn	Agbenin and Olojo, 2004
Acid soils of Cáceres (Spain)	Pb > Cd	Serrano et al., 2005
Acid soils of Galicia (Spain)	Cu > Zn	Arias et al., 2006
Soil of north eastern France	Cr > Cu > Zn	Flogeac et al., 2007
Soils of western Iran	Cu > Zn > Cd > Ni > Mn; Cu > Ni > Zn > Cd > Mn; Cu > Cd > Zn > Ni > Mn;	Jalali and Moharrami, 2007
Soils developed on shale in Egypt	Pb > Cu > Zn > Ni > Cd	Usman, 2008
Fibric Histosol of Pontevedra (Spain)	Cr ≈ Pb >> Cu >> Cd > Zn ≈ Ni	Covelo et al., 2008
Soil of Porquerolles Island (France)	Cr > Pb > Cu	Merdy et al., 2009
Soil of South Spain	Pb > Cu > Zn > Cd	Vidal et al., 2009

1.2.3.3 Inorganic and organic ligands

Many inorganic and organic ligands, such as phosphate, sulfate, carbonate, chloride and oxalate, tartrate, citrate, phthalate, salicylate, are present in soil, especially in the rhizosphere. These anionic ligands, which originate from natural activity, fertilizer application, organic mater decomposition, plant root or microorganism secretion, play a vital role in various interfacial interactions, including the sorption of trace elements. The sorption of cationic trace elements could be facilitated, depressed or unchanged in the presence of anionic ligands.

Several mechanisms based on macroscopic and spectroscopic investigations have been proposed to explain the enhancement of cationic trace elements by the presence of anionic ligands: (1) the formation of ligand-metal-surface (type A) or metal-ligand-surface (type B) ternary complexes (Lamy et al, 1991; Ali and Dzombak, 1996; Ostergren et al, 2000a; 2000b); (2) electrostatic effect, the sorption of negatively charged anions could reduce the positive charges of mineral surface and result in more attractive surface for the sorption of heavy metals, the phenomena is defined as electrostatic effect if there is no formation of ternary surface complexes (Diaz-Barrentos et al., 1990; Collins et al., 1999); (3) the combination of both above mechanisms (Elzinga et al. 2001; Zhang and Peak, 2007); (4) the formation of surface precipitates (Collins et al. 1999). On the other hand, the formation of soluble metal-ligand complexes and the competition between cations and anions for sorption sites have been suggested as the explanation for the reduction of cationic trace element sorption by the presence of anionic ligands (Buerge-Weirich et al., 2003; Li et al., 2006).

The effect of anionic ligands on the sorption of cationic trace elements by soil components could be influenced by solution pH and the nature of soil components. Pretreatment by phosphate promoted the sorption of Cu and Cd on goethite while inhibited their sorption on hematite (Li et al., 2006; 2007). The sorption of both Cd and Zn by alumina increased at low pH range (< 6.5) while decreased at pH above 6.5 (Benyahya and Garnier, 1999). Lackovic et al. (2004) found that Cd sorption on kaolinite was promoted below pH 6.0 and decreased slightly above pH 6.5 in the

presence of 50 and 100 μmol L^{-1} citric acid. The crossover between enhancement and decrease was observed at pH 4.5 when the concentration of citric acid was increased to 1 mmol L^{-1}, moreover, these effects were more pronounced at higher citric acid concentration (Lackovic et al., 2004).

The influence of anionic ligands on the sorption of cationic trace elements by soil components could also be controlled by the concentration or species of trace element. The enhancements of the sorption of Pb and Cd and the retardance of Hg sorption on goethite in the presence of chloride have been found by Gunneriusson and Sjöberg (1993), Gunneriusson et al. (1994) and Gunneriusson (1994). Buerge-Weirich et al. (2003) showed that oxalate decreased the sorption of Cu and Ni on goethite at high pH regions but had no effect on Cd sorption. Ha et al. (2009) prepared two hematite with different particle size [hematite nanoparticles (HN) (average diameter = 10.5 nm) and hematite microparticles (HM) (average diameter = 550 nm)] to investigate the interaction of Zn, oxalate and hematite in ternary system. By keeping constant the initial concentration of oxalate (8 mmol L^{-1}), an increase in Zn uptake was found on HN when the concentration of Zn was higher than 2 mmol L^{-1}, while an inhibition in the sorption of Zn was observed on HM when the concentration of Zn was lower than 6 mmol L^{-1} (Ha et al., 2009).

The effect of anionic ligands on the sorption of cationic trace elements by soil components could be also controlled by the concentration or type of anionic ligand. Angove et al. (1999) revealed that Cd sorption (5×10^{-5} mol L^{-1}) on goethite was enhanced by benzene carboxylic acid and the sequence of phthalic (benzene-1,2-dicarboxylic acid) ≈ hemimellitic (1,2,3) < trimellitic (1,2,4) < trimesic (1,3,5) ≈ pyromellitic (1,2,4,5) < mellitic (1,2,3,4,5,6) in the degree of enhancement was observed by comparing the sorption edge in the absence and presence of 1×10^{-3} mol L^{-1} ligand. Low concentrations (0.04 mmol L^{-1}) of chelidamic acid enhanced the sorption of Cu on goethite (Ali and Dzombak, 1996). However, an increase trend at pH < 5 while an reduction tendency at pH > 5 in Cu sorption on goethite was observed with the raise of chelidamic acid concentration to 0.2 mmol L^{-1} (Ali and Dzombak, 1996). Huang et al. (2010) found that the presence of acetate, tartrate and

citrate at low concentrations (< 0.6 -1.0 mmol L^{-1}) facilitated the sorption of Pb on goethite at pH 5.0 while an inhibitive effect was investigated when the concentration of each ligand raised to 1.0-3.0 mmol L^{-1}. The observation of Song et al. (2008) revealed that the sorption of Cd and Cu on ferrihydrite was enhanced in all cases when the presence of phthalic acid was 0.6 mmol kg^{-1}, the sorption of Cd was still increased when the concentration of phthalic acid rasied to 6 mmol kg^{-1} while that of Cu was enhanced at pH < 5 and was depressed at pH > 5, with the further increase of ligand concentration to 30 mmol kg^{-1} in Cd system and 28 mmol kg^{-1} in Cu system, the sorption of Cd was enhanced in most conditions but was depressed at higher pH region, while that of Cu was dramatically depressed especially at higher and greater heavy metal/Fe ratio (0.025 mol/mol).

1.3 Characterization of trace elements sorption on typical soil complexes

As discussed above, phyllosilicates, Fe- or Al- oxides, humic substances and microorganisms are the most important soil components for scavenging trace elements. In natural environments, these components interact with each other through electrostatic interaction, hydrophobic interaction, hydrogen bonding, van der Waals force, covalent bonding and so on and form various complexes such as organo-mineral complexes, microorganism-mineral complexes, metal oxide-phyllosilicate complexes, Fe-Al mixed oxides. The mechanism and reactivity of these complexes in retaining heavy metals is different from those of the single components involved in the formation of complexes.

1.3.1 Sorption of trace elements on organo-mineral complexes

One type of organo-mineral complexes is formed by the interaction of humic substance which is macromolecular with mineral. The sorption properties of trace elements on this kind of complexes are complicated since the heterogeneous nature of the sorbents. Trace elements may be bound merely to the surface of mineral, or link functional groups of humic substance and mineral as bridges in the complexes (type A ternary complexes; Fig.3), or be bound to only humic substance which is retained

simultaneously on the mineral (type B ternary complexes; Fig.3) (McBride, 1994; Alcacio et al., 2001). The amount of humic substance in the organo-mineral complexes plays a vital role in affecting the sorption mechanism of trace elements. Analysis of the XANES and EXAFS data by Alcacio et al. (2001) revealed that Cu was bonded by type A ternary complexes when low amonts of humate were present while by type B ternary complexes when the loading levels of humate were higher.

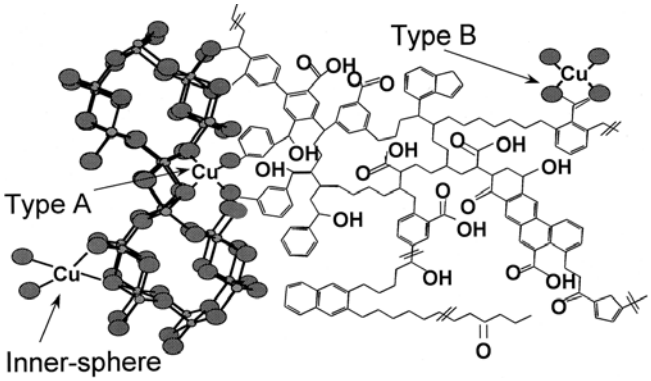

Fig.3. Possible bonding configurations of Cu on goethite-humate complexes: inner-sphere complexation of Cu at goethite sites, and type A and B ternary complexes (Alcacio et al., 2001)

The actual sorption amounts of trace elements on humic substance-oxide complexes are not equal to the sum of their sorption on isolated components. Due to the interaction between the negatively charged Aldrich humic acid and the positively charged hematite, Vermeer et al. (1999) pointed out that the adsorption of Cd on hematite in humic acid-hematite complexes was increased as compared to that on the isolated oxide, whereas Cd adsorption on humic acid in the complexes was decreased as compared to that on isolated humic acid. Moreover, the overall adsorption of Cd to the complexes was lower than predicted by the additivity rule when the metal had a more pronounced affinity for humic acid than for oxide (the case at low pH), while it was higher than predicted by the additivity rule when the metal had a more greater affinity for oxide than for humic acid (the case at high pH) (Vermeer et al., 1999). By comparing the binding of Cu on the purified Aldrich humic acid (PAHA)-goethite complexes with that on isolated sorbent in the neutral to acidic pH region, Saito et al. (2005) found that Cu binding in the ternary system was enhanced with respect to the

sum of its binding in the corresponding binary systems. Moreover, the authors pointed out that such increase of Cu binding was attributed mainly to the decrease of proton competition to the functional groups of the adsorbed PAHA and the change of the electrostatic potential in the vicinity of goethite surface (Saito et al., 2005).

The coating of humic acid on mineral could also affect the formation of precipitates of trace elements. Batch and EXAFS observation by Nachtegaal and Sparks (2003) showed that the uptake kinetics and capacity of Ni on kaolinite increased with the amount of humic acid (HA) coating, but the formation of surface precipitate was slowed significantly with a higher amount of HA coating. Moreover, the precipitate formed in the presence of a 5 wt % HA coating was Ni hydroxide while a more stable Ni-Al LDH was formed in the presence of 1 wt % HA coating (Nachtegaal and Sparks, 2003).

Low molecular weight organic acids, such as oxalic, tartaric and citric acid, which are abundant in soil environment especial in the rhizosphere, may interact with Fe or Al species and facilitate the formation of another type of organo-mineral complexes (Violante and Gianfreda, 2000; Huang, 2004). The organic ligands in this type of orgno-mineral complexes not only can be adsorbed on the external surface, but also can be incorporated into the structural network of the oxides (Liu and Huang, 2003). The surface properties of this type of organo-mineral complexes thus are different from the first type. The point zero salt effect (PZSE) or the point of zero charge (PZC) is generally decreased with the increase of the amount of organic ligands in organo-mineral complexes (Xue and Huang, 1995; Liu and Huang, 2003; Yu et al., 2006). On the other hand, the surface area could be increased or decreased, depending on the species of Fe [Fe(II), Fe(III)] or Al and the molar ratio (MRs) of ligand to Fe or Al species. Yu et al. (2006) found that the surface area of Al oxide formed in the absence or presence of tannate increased with the increase of the amount of ligand in the sample. Xue and Huang (1995) found that the surface area of the sample formed by precipitating Fe(III) in the presence of citric acid (MRs = 0.1) was lower than that formed in the absence of citric acid. By precipitating Fe(II) with increasing amounts of citrate (MRs = 0, 0.001, 0.01, 0.1), Liu and Huang (2003)

found that the surface area of the samples followed the sequence of 0.1 > 0.01 ≥ 0 > 0.001. According to the observations of Xue and Huang (1995), Liu and Huang (2003) and Yu et al. (2006), the sorption of Zn, Pb and Cd on Fe- or Al- oxides was promoted with increasing the incorporation of organic ligands.

1.3.2 Sorption of trace elements on microorganism-mineral complexes

Microorganism-mineral complexes, which form by electrostatic or hydrophobic interaction between microorganisms and minerals, are other types of common complexes in natural environments (Huang et al, 2005). The sorption sites for trace elements in individual component could be occupied, masked or neutralized by their interaction. Physicochemical interaction of *Escherichia coli* cell envelopes and *Bacillus subtilis* cell walls with two clays and the ability of the composite to immobilize cationic trace elements have been investigated by Walker et al. (1989). About 20-90% of the reductions of metal binding on the envelope-clay (envelopes plus smectite, envelopes plus kaolinite) and wall-clay (walls plus smectite, walls plus kaolinite) mixtures compared to that on the equal amounts of the individual components were observed (Walker et al., 1989). Similarly, less sorption capacities of Cd and Pb on the composites of ferrihydrite with *B. subtilis* or *E. coli* than the sorption capacities which predicted by their individual sorption values have been reported by Kulczycki et al. (2005). In Cd-ferrihydrite-bacteria (*Comamonas* spp.) systems, the adsorption of Cd was also up to 10% lower than that predicted by additive adsorption onto the pure phases (Song et al., 2009).

The investigation on the sorption of trace element on microorganism-mineral complexes was furthered by the observation on their distribution on the heterogeneous complexes. The ratios between microorganism and mineral, the concentrations of examined metal, the pH of the system are the potential factors in affecting the distribution of trace elements. The significance of bacterial surface in the adsorption of Cd was clearly indicated by decreasing the ferrihydrite-*Comamonas* spp. (dry weight) ratio from 10 to 2 (Song et al., 2009). By observing the distribution of Pb on biofilm-metal oxide interfaces as a function of Pb concentration from 10^{-7} to $10^{-3.8}$

mol L^{-1}, Templeton et al (2001) found that high-energy surface sites on the metal oxides was the dominant sink for Pb at submicromolar concentrations, following the trend *a*-Fe_2O_3 (0001) > *a*-Al_2O_3(1$\bar{1}$02) > *a*-Al_2O_3(0001), while significant Pb uptake by the biofilms was observed at [Pb] > 10^{-6} mol L^{-1}. Molecular evidences from EXAFS studies showed that the dominant sorbent in *Burkholderia cepacia*/goethite composites switched from the biofilm at low pH to the goethite surface at higher pH (Templeton et al, 2003). The preferential sorption of Pb to the biofilm at lower pH could be ascribed to the lower pK_a values of functional groups on bacteria surface (eg. carboxyl, phosphate) than that of functional group on goethite surface (hydroxyl) (Templeton et al, 2003).

1.3.3 Sorption of trace elements on metal oxide-phyllosilicate complexes

Metal oxide-phyllosilicate complexes, including Al oxide-phyllosilicate, Fe oxide-phyllosilicate and Mn oxide-phyllosilicate complexes, occur commonly in acid to slightly acid soils with a wide geographic distribution. However, most investigations on the adsorption of cationic trace elements by these types of complexes are focused on $Al(OH)_x$-montmorillonite complexes. The pH of the system plays an important role in affecting the sorption of trace elements on $Al(OH)_x$-montmorillonite complexes. The presence of Al polymers on montmorillonite promoted the adsorption of cationic trace elements at higher pH (Lothenbach et al., 1997; Saha et al., 2001, 2002; Janssen et al., 2003; 2007), since the available binding sites on Al polymers have strong affinity for cationic trace elements (Janssen et al., 2003; 2007). However, aluminum coated montmorillonite was usually less efficient than untreated montmorillonite in immobilizing cationic trace element at low pH (Lothenbach et al., 1997; Janssen et al., 2003; 2007), Janssen et al. (2003; 2007) proposed three explanations for this observation: (1) a significant fraction of exchangeable aluminum ions present on the clay surface at low pH, (2) the concentration of local protons near the surface of Al polymers is also higher when the pH is low, the binding of cationic trace element on clay or Al polymers was inhibited by the competition from exchangeable aluminum ions or local protons, (3) the

reduction of CEC of clay was also greater at low pH with the same loading of Al polymers due to the higher positive charge of the polymers at lower pH.

Both nonspecific sorption and specific sorption have been suggested as the mechanisms of trace element sorption on montmorillonite. In contrast, highly specific sorption was usually implied for trace element sorption on $Al(OH)_x$-montmorillonite complexes by macroscopic investigation, since the reduction of CEC by the attachment of Al polymer and the incorporation of trace element into the interlayer hydroxyl-Al polymer (Harsh and Doner, 1984; Sakurai and Huang, 1996; Saha et al., 2001; Janssen et al., 2003). Spectroscopic investigations by EXAFS confirmed the incorporation of trace elements in vacant octahedral sites of gibbsite-like layers at the basal and/or interlayer surface of montmorillonite (Nachtegaal et al, 2005; Schlegel and Manceau, 2007). An exception found by Lothenbach et al. (1998) was that the binding of Cd was essentially nonspecific on $Al(OH)_x$-montmorillonite complexes although the opposite behavior was found for Zn.

Compared to Al oxide-phyllosilicate complexes, few attention has been paid to the adsorption of cationic trace elements on Fe oxide-phyllosilicate complexes. Ferrihydrite-montmorillonite (Fe-Mont) and lepidocrocite-montmorillonite (Lep-Mont) were synthesized by Green-Pedersen and Pind (2000) to investigate the sorption properties for Ni. A completely coated form of ferrihydrite in Fe-Mont and a separate phase of lepidocrocite in Lep-Mont were revealed by analyzing the reorganization, surface area, PZC and TEM image of the particles (Green-Pedersen and Pind, 2000). The binding capacity of Fe-Mont and Lep-Mont for Ni were both higher than that of pure montmorillonite with equal mass of sorbent, however, Fe-Mont showed a similar sorption capacity to pure ferrihydrite while Lep-Mont showed lower sorption capacity than that of pure lepidocrocite due to their difference in reorganization of the particles (Green-Pedersen and Pind, 2000).

The sorption capacity and affinity of Mn oxides for cationic trace elements are usually greater than that of Al and Fe oxides (Trivedi and Axe, 2000). However, the attention to the behavior of cationic trace elements on Mn oxide-phyllosilicate complexes is also scant. Boonfueng et al. (2006a, 2006b) have compared the sorption

behaviors of Zn, Ni and Pb on montmorillonite, hydrous Mn oxide (HMO) and HMO-coated montmorillonite. The sorption affinity and capacity of HMO-coated montmorillonite for Zn were greater than that of pure montmorillonite (Boonfueng et al., 2006a; 2006b). The coated HMO behaved similarly to the discrete Mn oxide in immobilizing Zn, Ni and Pb, octahedral coordination, tridentate or bidentate corner sharing complexes were suggested by XAS analysis as sorption mechanisms on discrete or coated HMO (Boonfueng et al., 2006a; 2006b).

1.3.4 Sorption of trace elements on Fe-Al mixed oxides

Both Fe and Al oxides are very effective in scavenging trace elements due to their high specific areas and reactive surface functional groups (Kinniburgh et al, 1976; Potter and Yong, 1999). Moreover, these oxides are ubiquitous in soils and sediments as discrete solids, coatings on other particles and particularly mixed oxides (Potter and Yong, 1999). The difference between Fe-Al binary oxide and their component parts in surface properties and sorption characteristics towards trace elements have been investigated by several researchers (Anderson and Benjamin, 1990a, 1990b; Potter and Yong, 1999; Violante et al, 2003). The sorption of Cd on Al-Fe binary suspensions was lower than that on $Fe(OH)_3$-only suspension while the opposite trend was observed for Zn (Anderson and Benjamin, 1990a). The following explanations were proposed by the authors: (1) Iron(III) precipitates at lower pH than Al(III) (Stumm and Morgan, 1996), previously agglomerated $Fe(OH)_3$ was redispersed by $Al(OH)_3$ which formed latterly, aluminum became relatively enriched on the surface of $Fe(OH)_3$ particles and controlled the chemical reactions on the surface of the particles (Anderson and Benjamin, 1990a), (2) less sorption of Cd on $Al(OH)_3$ than that on $Fe(OH)_3$ and approximate equal sorption of Zn on $Al(OH)_3$ and $Fe(OH)_3$ thus resulted in the difference of their sorption on Al-Fe binary and $Fe(OH)_3$-only suspension (Anderson and Benjamin, 1990a). The retention of Pb and Cu on amorphous Fe, Al and mixed Fe-Al oxides with different Fe/Al molar ratio has been investigated by Potter and Yong (1999). Lead retention by mixed oxides at a particular pH increased with Fe/Al ratio in the order Fe > 3FeAl > FeAl > Fe3Al > Al

(□3FeAl□ stands for Fe/Al molar ratio = 3; □FeAl□ stands for Fe/Al molar ratio = 1; □Fe3Al□ stands for Fe/Al molar ratio = 0.3), the same order was found for Cu at low to medium concentration (0.5, 2.5, 5 mmol L^{-1}) while only Fe oxide has a clearly greater retention capacity when the loading of Cu was higher (25 mmol L^{-1}). The sorption of Cu, Pb, Zn and Co on mixed Fe-Al oxides which were prepared by precipitating mixtures of Fe and Al ions at pH5.5 with initial Fe/Al molar ratios (R) of 0, 1, 2, 4, 10 and ∞ has been studied by Violante et al (2003), it was found that the greater the amounts of Fe in Fe-Al gels, the lower the pH_{50} for each metal, suggesting the higher the sorption affinity, but there was no linear relationship between the sorption of trace elements and the content of Fe in the mixed gels.

2. Aim of the Thesis

Extensive studies have investigated the sorption of heavy metals on phyllosilicates, metal oxides, organic substances and microorganisms in single sorbate or on single sorbent systems. However, to date, the sorption of heavy metals onto organomineral complexes and mineral-bacteria complexes has received only little attention. On the other hand, even though the competition in sorption among different heavy metals have been studied on most individual soil components and soils, scant attention has been devoted to the competitive sorption among heavy metals on organomineral and oxide-bacteria complexes.

Low molecular weight organic ligands have been reported to promote, inhibit or uninfluence the sorption of heavy metals by various clay minerals and soils. However, to date, scant attention has been paid to the effect of these anions on the sorption of heavy metals by bacteria. The competitive sorption of heavy metals on bacteria is also of great importance to understand the mobility of heavy metals in soils and deserves great attention.

Sorption of heavy metals on phyllosilicates has also received great attention, however, the information about the competitive sorption of heavy metals and the effect of cationic macroelement, such as Fe, Al, Ca and Mg, on their sorption by phyllosilicates such as montmorillonite is also scant.

The sorption of arsenate which is a typical anionic trace element on layered double hydroxides (LDHs) has received some attention. However, few studies paid attention to the influence of foreign ligands, such as phosphate, which presents commonly in soil and aquatic environment, on the sorption of arsenate by LDH.

The aim of this thesis was to investigate the sorption of heavy metals and metalloids added alone or as a mixture on selected soil components, such as ferrihydrite, goethite, bacteria, montmorillonite, LDHs minerals, organomineral and oxide-bacteria complexes as affected by pH, presence of low molecular weight organic ligands, sequence of element additions, residence time and surface coverage in order to have useful information on the factors which may affect their mobility. In particular, the following topics have been considered:

(1) Competitive sorption of Cu, Cr and Pb on ferrihydrite and two organomineral complexes;

(2) Biosorption of Cu, Cr and Pb on *Bacillus thuringiensis*: competition and the effect of low molecular organic ligands;

(3) Competitive sorption of Cu and Cr on goethite and goethite-bacteria complex;

(4) Sorption of Cu, Cr and Pb on Na-Montmorillonite: Competition and the effect of macroelements;

(5) Sorption/desorption of arsenate on/from Mg-Al layered double hydroxides: Influence of phosphate.

3. Competitive Sorption of Cu, Cr and Pb on Ferrihydrite and two Organomineral Complexes

3.1 Materials and methods

3.1.1 Syntheses and characterization of ferrihydrite and organomineral complexes

Ferrihydrite was prepared by precipitating 0.1 mol L^{-1} $Fe(NO_3)_3$ at pH 5.5 with 0.5 mol L^{-1} NaOH added slowly at a rate of 0.5 ml min^{-1} (Cornell and Schwertmann, 1996). The final volume was adjusted to 1 L. For the two organomineral complexes, fresh stock solutions of 0.1 mol L^{-1} $Fe(NO_3)_3$, tartrate and oxalate were prepared in order to have an initial (tartrate + oxalate)/Fe molar ratio (R) of 0.1 and 0.2, named Fe(OH)OL1 and Fe(OH)OL2, respectively. These solutions were titrated with 0.5 mol L^{-1} NaOH at a rate of 0.5 mL min^{-1} while stirring to pH 5.5. After 24h, the suspensions were washed with distilled deionized water, freeze-dried and ground to pass through a 0.315 mm sieve.

The surface area of the samples was measured by H_2O sorption at 20 % relative humidity as described by Quirk (1955). The point of zero charge (PZC) of the samples was determined by laser doppler velocimetry-photon correlation spectroscopy (Beckham Coulter Electronics, Hialeah, FL).

For iron determination, suitable amount of each sample was digested in a microwave (Milestone Digestor/Dring Ethos 900). The samples were accurately weighed into a PTEE pressure vessel in the presence of HNO_3 (65 %) solution. Total iron concentration was determined by atomic absorption spectrometry (Perkin-Elmer A Analist 700). An elemental analyzer (EA 1108, Fison) was used to determine the content of organic carbon in organomineral complexes.

The samples were further characterized by X-ray diffraction (XRD) and FT-IR as described by Pigna et al. (2006), using a Rigaku diffractometer (Rigaku Corporation, Tokyo) and a Perkin-Elmer Spectrum One FT-IR spectrophotometer (Perkin-Elmer USA), respectively.

3.1.2 Sorption isotherms and kinetics

Fifty milligram of each sorbent, previously dried at 100 °C for 1 h, were mixed with 19.7 ml of 0.02 mol L^{-1} KNO_3 containing 1-20 μmol of Cu, Cr and Pb individually in a series of 50 mL conical flasks. The mixtures were shaken at 20°C for 4 h and the pH of each suspension was kept constant at 4.5 by the addition of 0.1 mol L^{-1} KOH or HNO_3 solution by an automatic titrator (Potentiograph E536 Metrom Herisau) in conjunction with an automatic syringe (burette 655 Dosimat). The final volume of each suspension was adjusted to 20 ml. The final suspension was centrifuged at 10,000 *g* for 20 min and filtered through Nalgene acetate membrane (pore size < 0.2 μm). The concentration of heavy metal in the final solution was determined by atomic absorption spectrometry. The sorption of heavy metal was calculated by the difference between the amount of heavy metal added initially and that remained in the supernatant.

Sorption kinetics was conducted at pH 4.5 by observing the sorption of each heavy metal on the sorbent from 0.5 to 24 h with initial addition dosage of 100 mmol heavy metal per kg of sorbent.

3.1.3 Effect of pH on the sorption

Sorption was conducted in the range of pH from 4.0 to 6.0. The samples were prepared as described before, but 10 μmol of individual heavy metal was employed, to result in an initial concentration of 200 mmol of each metal per kg of sorbent. The suspensions were shaken at 20° C for 4 h and their initial pH was kept constant. The supernatant of each sample was collected and the concentration of the heavy metals was determined as described above.

3.1.4 Competitive sorption in binary and ternary systems

Competitive sorption of Cu, Cr and Pb in binary systems was observed at pH 4.5 by adding Cu and Cr, Cu and Pb or Cr and Pb as a mixture to the sorbents, keeping the concentration of a selected metal (M1) constant at 100 mmol kg^{-1} and that of the other metal (M2) ranging from 0 to 300 mmol kg^{-1} in order to have an initial M2/M1

molar ratio (ri) of 0, 1, 2 or 3. Some experiments were also carried out by adding M1 to the sorbent 1 h or 24 h before the addition of M2.

Competitive sorption of Cu, Cr and Pb in ternary systems was investigated by adding Cu, Cr and Pb as a mixture to the sorbents. The concentration of each metal was 100 or 200 mmol kg^{-1} to have an initial molar ratio Pb: Cr: Cu of 1:1:1, 1:1:2, 1:2:1, 2:1:1 or 2:2:2.

The pH of each suspension was kept constant at 4.5 for 4 h. The supernatant was collected and the concentration of the heavy metals was determined as described above.

Negligible dissolution of ferrihydrite and organomineral complex was detected in this study.

3.2 Results

3.2.1 Nature of the sorbents

The sample prepared in the absence of organic ligands showed an X-ray diffraction pattern with very diffuse peaks around 0.250, 0.225 and 0.150 nm, characteristic of ferrihydrite (Cornell and Schwertmann, 1996; Violante and Gianfreda, 2000; Pigna et al., 2006), whereas the organomineral complexes were non-crystalline. FTIR analyses confirmed the nature of these materials (Fig. 4). The organomineral complexes showed bands around 1670 cm^{-1}, characteristic of C=O stretching vibrations in anionized COOH carboxylic groups and around 1400 cm^{-1} representing ionized COO^- carboxylate group. The bands observed around 1300 and 1070 cm^{-1}, resulted from C-C stretching vibrations and C-H deformations in organic ligands (Öhrström and Michaut-Soret, 1999).

The surface area, PZC and chemical composition of the samples are reported in Table 7. The content of iron in the samples decreased from 692 g kg^{-1} in ferrihydrite to 639 g kg^{-1} in Fe(OH)OL2, whereas the two organomineral complexes had a carbon content of 15 g kg^{-1} [Fe(OH)OL1] and 23 g kg^{-1} [Fe(OH)OL2]. Ferrihydrite showed a surface area of 599 m^2 g^{-1} and a PZC of 7.45. In sharp contrast, the two organomineral complexes had substantially lower surface area and PZC, which were 363 m^2 g^{-1} and

5.10 for the Fe(OH)OL1 and 350 m^2 g^{-1} and 4.14 for the Fe(OH)OL2, respectively. The reduction of surface area of the sorbents as a result of increasing the carbon content was predominantly due to the aggregation of the Fe-oxide particles promoted by organic ligands (Violante and Huang, 1989; 1992; Violante and Gianfreda, 2000). Violante and Huang (1989; 1992) demonstrated that polydentate organic ligands played an important role in promoting the formation of short-range ordered materials versus crystalline Al- or Fe- oxides and facilitating, particularly above certain concentrations, the aggregation of the particles of the precipitates. Oxalate and tartrate strongly sorbed on Fe precipitation products made the surfaces less positive, thereby lowering the pH value for PZC at which the surface charge becomes zero. Lowering of PZC of metal oxides after sorption of organic and inorganic anions forming inner sphere complexes on their surfaces have been widely demonstrated (Violante and Huang, 1992; Violante and Gianfreda, 2000; Li et al., 2006; 2007).

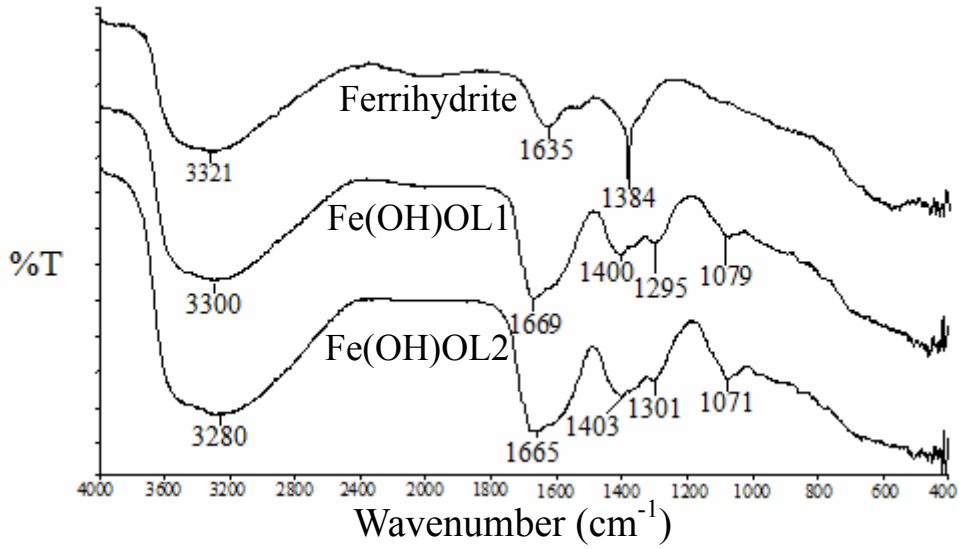

Fig.4. FTIR spectra of ferrihydrite and organomineral complexes

Table7 Basic properties of ferrihydrite and organomineral complexes

	Surface area (m^2 g^{-1})	PZC	Carbon content (g kg^{-1})	Iron content (g kg^{-1})
Ferrihydrite	599 ± 13	7.45 ± 0.21	----	692 ± 15
Fe(OH)OL1*	363 ± 8	5.10 ± 0.12	15 ± 0.4	664 ± 24
Fe(OH)OL2*	350 ± 16	4.14 ± 0.10	23 ± 0.6	639 ± 20

*Fe(OH)OL1 and Fe(OH)OL2 stand for the organomineral complexes obtained by precipitation of $Fe(NO_3)_3$ in the presence of oxalic (OX) and tartaric (TA) acids at an (OX + TA)/Fe molar ratio of 0.1 and 0.2, respectively. Initial OX/TA molar ratio was 1.0.

3.2.2 Sorption kinetics

Through various sorption experiments, we observed that overall affinity and capacity (μmol m^{-2}) of metal sorption on the three sorbents of this study followed the order of Fe(OH)OL2 > Fe(OH)OL1 > ferrihydite. Therefore, in this paper, comparative evaluation of the sorbents with respect to most of the sorption phenomena (e.g., sorption isotherms, sorption kinetics and competition among the metals for sorption) was done using ferrihydite and Fe(OH)OL2 only. Figure 5 shows the sorption kinetics of Cu, Cr and Pb on ferrihydite and Fe(OH)OL2. A steady increase within the first 2 h of reaction followed by an appreciable stabilization trend from 2 h to 8 h was observed for the sorption of heavy metals on both sorbents. Only a slight increase (4-10%) in the sorption with further extension of the residence time up to 24 h was found. A number of studies have shown that heavy metal sorption on oxides was initially fast, followed by a very slow sorption reaction (Borda and Sparks, 2008). The mechanisms of this slower reaction was not well understood, but have been ascribed to inter- and intra-particle diffusion phenomena, sorption to the sites of lower reactivity and to surface nucleation-precipitation (Borda and Sparks, 2008). For sorption studies a reaction time of 4 h was then chosen.

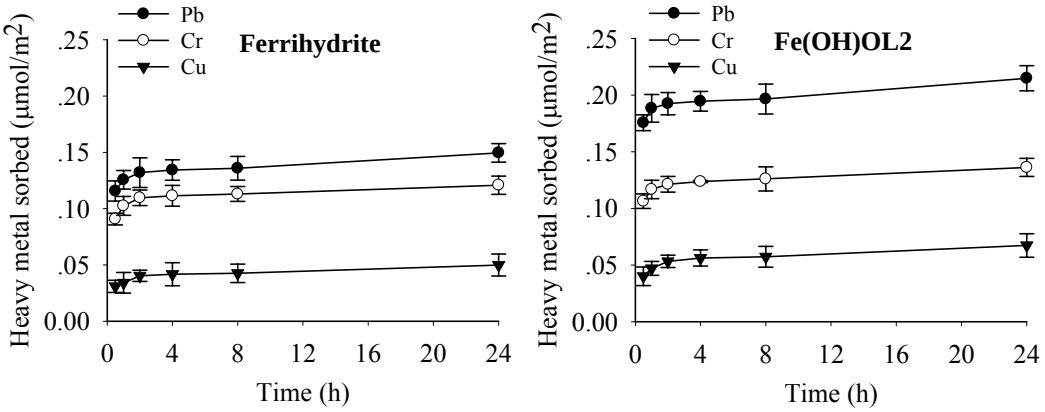

Fig.5. Sorption kinetics of Cu, Cr and Pb on ferrihydrite and Fe(OH)OL2 at pH 4.5.

3.2.3 Sorption isotherms

The sorption isotherms of Cu, Cr and Pb added individually onto ferrihydrite and Fe(OH)OL2 at pH 4.5 are shown in Fig. 6. The sorption data conformed to the Langmuir equation: $X = X_m KC/(1+KC)$, where X is the amount of each metal sorbed per unit mass of sorbent (mmol/kg or μmol/m^2), X_m is the maximum amount that may be bound to the sorbent (sorption capacity), C is the equilibrium solution concentration (mmol L^{-1}), and K is a constant related to the binding energy. Greater K values indicate higher affinity between a heavy metal and a sorbent (Sparks, 2002).

The isotherms of Cu and Cr on both ferrihydrite and Fe(OH)OL2 belonged to L-type (Fig. 6A-D). In contrast, the shape of the isotherms of Pb sorbed particularly on Fe(OH)OL2 indicated a high affinity behavior (H-type). The higher affinity of heavy metals for the organomineral complexes compared to that for ferrihydrite was also revealed by the higher K values reported in Table 8. These results were ascribed to the presence of oxalate and tartrate in organomineral complexes, which rendered the surface of the precipitates more negative (Table 7) and provided many supplementary available sites with high affinity for the heavy metals (Senesi and Loffredo, 2008; Violante et al., 2008). Copper, Pb, and Cr forms very stable complexes with oxalic and tartaric acid (Violante et al., 2003). It was noteworthy that the amounts of Cu, Cr and Pb sorbed on ferrihydrite were much higher than that retained on Fe(OH)OL1 (data not shown) and Fe(OH)OL2 when the scale of mmol

per kg was considered (Fig.6A, 6C, 6E; Table 8), owing to the larger surface area of ferrihydrite. However, the opposite trend was observed when the scale of μmol per m^2 was taken into account (Fig.6B, 6D, 6F; Table 8). This behavior was probably due to the higher density of sorption sites on organomineral complexes, which was induced by the aggregation of the particles in the presence of organic ligands as discussed above.

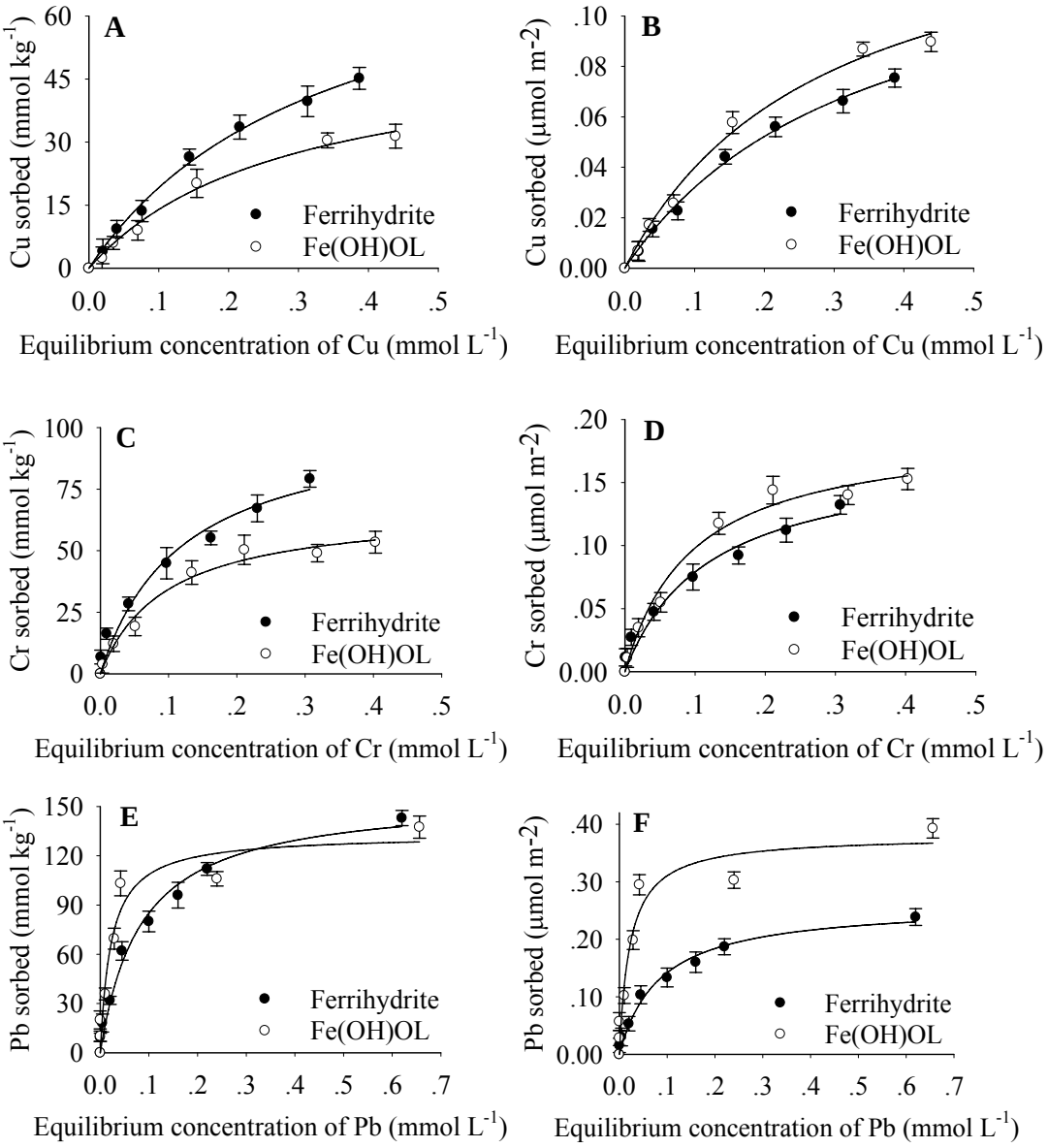

Fig.6. Sorption isotherms of Cu, Cr and Pb on ferrihydrite and Fe(OH)OL2 at pH 4.5.

Table8 Langmuir parameters for the sorption of Cu, Cr and Pb on ferrihydrite and Fe(OH)OL2

Heavy metal	Sorbent	X_m (mmol kg^{-1})	X_m (μmol m^{-2})	K	R^2
Cu	Ferrihydrite	85.1	0.1421	2.9	0.99
	Fe(OH)OL2	53.7	0.1534	3.5	0.99
Cr	Ferrihydrite	104.1	0.1738	8.3	0.97
	Fe(OH)OL2	67.3	0.1923	10.4	0.98
Pb	Ferrihydrite	156.6	0.2614	11.9	0.98
	Fe(OH)OL2	132.9	0.3796	44.8	0.94

3.2.4 Effect of pH on the sorption of Cu, Cr and Pb

The quantities of Cu, Cr and Pb sorbed on ferrihydrite and Fe(OH)OL2 (expressed as percentage of the amount initially added, 200 mmol kg^{-1}) increased with the increase of pH (Fig. 7). The pH value at which 50% of the amount of a given heavy metal is sorbed is called pH_{50}. According to many authors, the lower the pH_{50} value the higher the affinity of a metal for the sorbent (Kinniburgh et al., 1976; Violante et al., 2003; Qin et al., 2006). The pH_{50} values of Cu, Cr and Pb on ferrihydrite (5.8, 5.0, 4.4, respectively) were higher than that on Fe(OH)OL2 (5.4, 4.9, 4.0, respectively), conforming the observation that heavy metals were sorbed more strongly onto the organomineral complex than ferrihydrite. Furthermore, the pH_{50} values also indicated that the affinity of heavy metals for both ferrihydrite and organomineral complexes followed the sequence of Pb > Cr > Cu.

By plotting the amounts of Cu, Cr and Pb sorbed on the Fe precipitates as μmol m^{-2} versus pH, higher amounts of heavy metals were retained on organomineral complexes [Fe(OH)OL2 more than Fe(OH)OL1] than that on ferrihydrite (data not shown). Figure 7D shows the sorption of Pb on the three sorbents, confirming that in the whole range of studied pH, greater sorption of Pb was induced by increasing the content of organic carbon in organomineral complexes (Table 7). The decrease of PZC of the organomineral complexes also facilitated the sorption of metal cations.

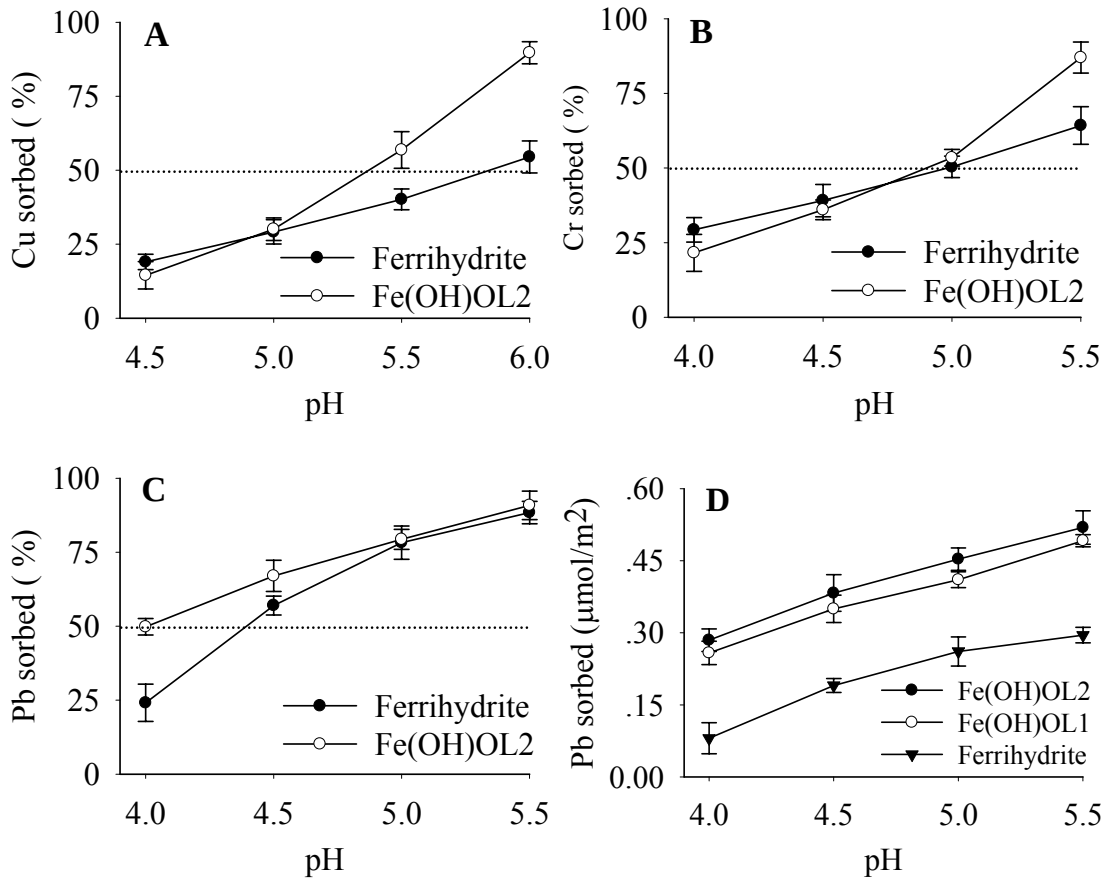

Fig.7. Effect of pH on the sorption of Cu (A), Cr (B) and Pb (C) (200 mmol kg^{-1}) by ferrihydrite and Fe(OH)OL2 and Pb sorption (D) on ferrihydrite, Fe(OH)OL1 and Fe(OH)OL2

3.2.5 Competitive sorption of heavy metals in binary systems

Competitive sorption of heavy metals was studied first in binary systems. Figure 8 shows the amounts (µmol m^{-2}) of Cu, Cr, or Pb (M1) sorbed on ferrihydrite and Fe(OH)OL2 at pH 4.5 when added alone (100 mmol/kg) or along with the competing metal (M2) in the binary systems of Cu-Cr, Cu-Pb and Cr-Pb with increasing initial M2/M1 molar ratios ranging from 0 to 3. The efficiency of a competing metal (M2) in inhibiting the sorption of a selected metal (M1) was calculated according to the following equation: Inhibitive efficiency of M2 (%) = (1 - M1 sorbed in the presence of M2/ M1 sorbed alone) ×100.

In the Cu-Cr systems, with increasing the initial Cr/Cu molar ratio from 1 to 3, the sorption of Cu was prevented by Cr on both ferrihydrite (from 39 to 64%) and

Fe(OH)OL2 (from 33 to 59%). The same trend was observed for the effect of Cu on the sorption of Cr, but Cu was less effective than Cr in preventing its sorption on both ferrihydrite (26-34%) and Fe(OH)OL2 (20-31%). Addition of equimolar amounts of Cu and Cr as a mixture (*Cu-Cr system*, initial Cr/Cu molar ratio of 1.0; Table 9), resulted in a final Cr/Cu molar ratio (rf) of 3.3 on ferrihydrite and 2.6 on Fe(OH)OL2, respectively, indicating that many sites on the sorbents, particularly on ferrihydrite, had a relatively stronger affinity and were more specific for Cr.

In the Cu-Pb systems, Cu poorly affected Pb sorption, especially on ferrihydrite. Even with an initial Cu/Pb molar ratio of 3, the sorption of Pb was reduced by only 19% on ferrihydrite versus 30% on Fe(OH)OL2 (Fig. 8). On the contrary, Pb strongly inhibited Cu sorption on both sorbents but slightly weaker on Fe(OH)OL2. This behavior must be attributed to the strong complexes that Cu may form with tartrate and oxalate on the organomineral complexes (Senesi and Loffredo, 2008). Furthermore, it was interesting to note that even at initial Pb/Cu molar ratio of 3.0, low amounts of Cu sorption (about 8 and 7 mmol kg^{-1}; 13.5×10^{-3} and 19.4×10^{-3} μmol m^{-2}) still occurred on both ferrihydrite and Fe(OH)OL2 although the sorption of Cu was strongly prevented by Pb, indicating that some sites on both sorbents were highly specific for Cu.

In the Cr-Pb systems, the efficiency of Pb in preventing Cr sorption was stronger on Fe(OH)OL2 (42-62%) than that on on ferrihydrite (11-55%) (Fig. 8). A similar difference between Fe(OH)OL2 and ferrihydrite was observed for Cr in inhibiting Pb sorption, but the efficiency of Cr in preventing Pb sorption was much lower than that of Pb in preventing Cr sorption. However, Cr was more efficient than Cu in competing with Pb on both the sorbents. Particularly on ferrihydrite, the low inhibition (11%) of Pb by Cr (and vice versa) at initial Pb/Cr molar ratio of 1.0 (Fig. 8) and the low rf value of 1.2 for Pb/Cr sorption (Table 9) was probably due to the fact that many sites were available for both the metals at relatively low concentrations (Fig. 6).

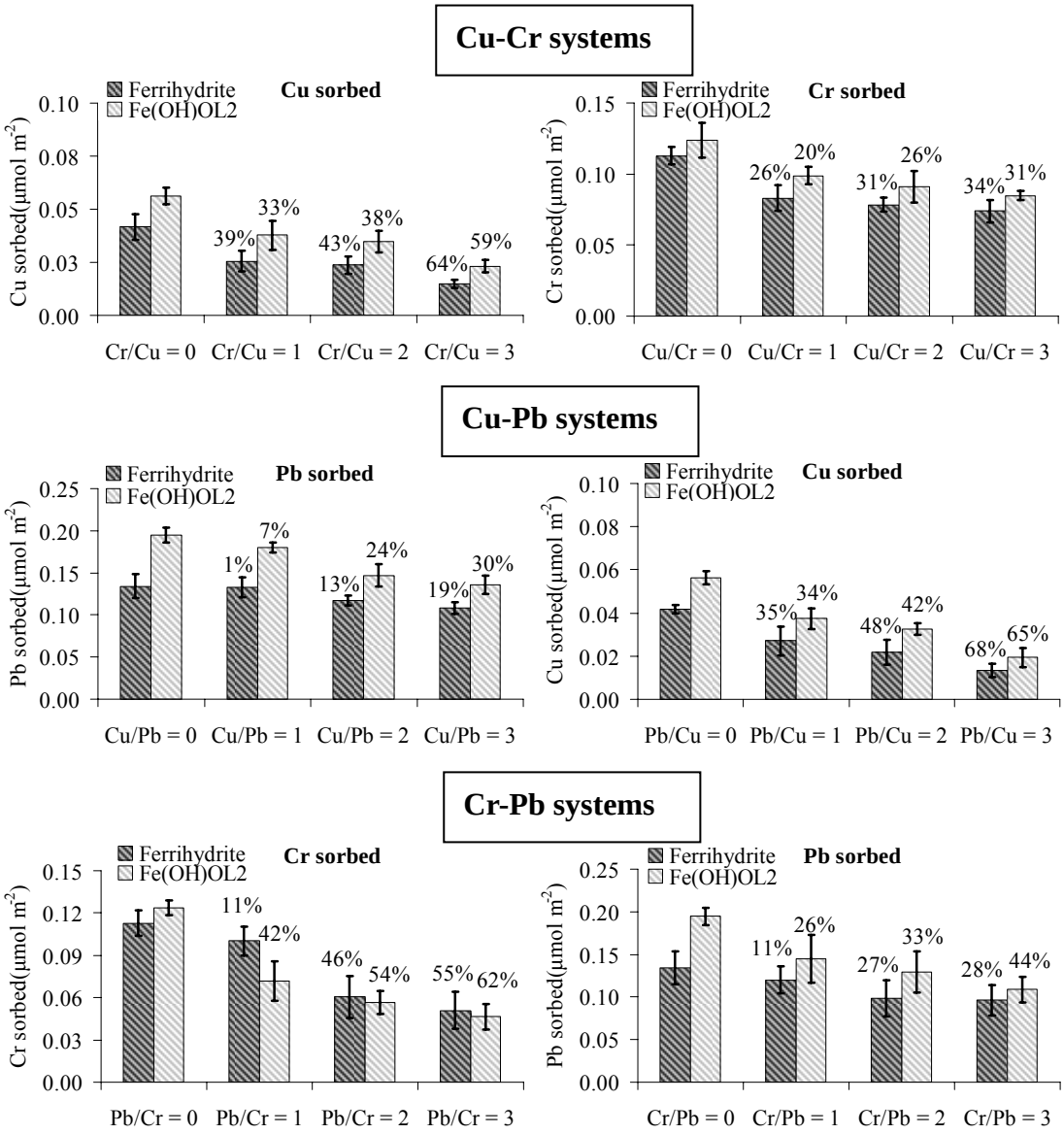

Fig.8. Amounts of Cu, Cr and Pb (M1) sorbed on ferrihydrite and Fe(OH)OL2 at pH 4.5 in the absence or presence of increasing concentration of a competing metal (M2) in binary systems (Cu-Cr, Cu-Pb or Cr-Pb) at initial M2/M1 concentration ratio of 0, 1, 2, and 3. The percentage values on the columns indicate the inhibitive efficiency of M2 in preventing M1 sorption.

3.2.6 Effect of addition sequence and residence time on competition in sorption of heavy metals

The sorption of heavy metals on ferrihydrite and Fe(OH)OL2 in binary systems was also affected by their addition sequence and the residence time (Table 9). The observations were conducted as following cases: i) a selected metal (M1) was added

to each sorbent simultaneously with a competing metal (M2) in equimolar concentrations (*M1-M2 system*), ii) M1 was added 1 h (*M1//M2-1h*) or 24 h before M2 (*M1//M2-24h*), and iii) vice-versa, M2 was added 1 h (*M2//M1-1h*) or 24 h before M1 (*M2//M1-24h*). The sorption of M1 in the presence of M2 usually decreased according to the following sequence: *M1//M2-24h* > *M1//M2-1h* > *M1-M2* > *M2//M1-24h* > *M2//M1-1h*, suggesting that greater amounts of M1 were sorbed when it was introduced alone earlier as compared to when added simultaneously as a mixture of M1+M2 or after the addition of M2. This behavior cannot be explained by taking in account only the kinetic of reactions (Fig. 5) but considering that a cation added first has the possibility to be easily sorbed on the sites of higher affinity. Thus, Cu, Cr or Pb was sorbed in greater amounts when added before the competing metal, as referred to the amounts sorbed in M1 + M2 systems.

Surprisingly, the sorption of Cu, Cr or Pb (M1) were slightly lower when they were added 1 h than 24 h after the competing metal M2 (*M2//M1-1h* systems versus *M2//M1-24h* systems) (Table 9). These findings probably implied the formation of precipitates on the surfaces of the sorbent with new sorption sites when the competing metal was loaded first and remained on the surfaces for longer period of time. In fact, it is well known that metal sorption on soil minerals often results in a continuum of transformation process from mere sorption (e.g. formation of outer- or inner-sphere complex) to precipitation (e.g. formation of mixed double metal hydroxide) with the increase of surface loading and residence time (Sparks, 2002; Borda and Sparks, 2008). The precipitate formed by the metal loaded earlier may create new sorption sites for the metal added subsequently.

Table 9 Sorption amounts ($\times 10^{-3}$ μmol m^{-2}) of Cu, Cr and Pb (100 mmol of each metal added per kg) in binary system on ferrihydrite and Fe(OH)OL2 as affected by the addition sequence and residence time

Cu vs Cr	Ferrihydrite			Fe(OH)OL2		
	Cu	Cr	Cr/Cu	Cu	Cr	Cr/Cu
Cu//Cr-24h	46.1 ± 2.1	79.8 ± 3.4	1.7 ± 0.1	58.0 ± 2.0	95.1 ± 3.8	1.6 ± 0.1
Cu//Cr-1h	32.4 ± 1.4	70.6 ± 2.6	2.2 ± 0.2	45.1 ± 1.8	91.7 ± 3.2	2.0 ± 0.1
Cu-Cr	25.5 ± 1.3	83.1 ± 2.9	3.3 ± 0.2	37.7 ± 2.0	98.9 ± 4.7	2.6 ± 0.1
Cr//Cu-1h	24.4 ± 1.5	85.5 ± 3.8	3.5 ± 0.1	30.9 ± 1.4	118.6 ± 3.8	3.8 ± 0.2
Cr//Cu-24h	30.2 ± 1.3	150.8 ± 5.6	5.0 ± 0.2	31.4 ± 1.1	128.6 ± 4.1	4.1 ± 0.2
Cu vs Pb	Ferrihydrite			Fe(OH)OL2		
	Cu	Pb	Pb/Cu	Cu	Pb	Pb/Cu
Cu//Pb-24h	44.7 ± 2.0	127.4 ± 3.0	2.9 ± 0.1	48.0 ± 1.6	178.6 ± 4.6	3.7 ± 0.2
Cu//Pb-1h	31.6 ± 1.3	120.2 ± 2.5	3.8 ± 0.1	43.4 ± 1.8	172.0 ± 5.2	4.0 ± 0.2
Cu-Pb	27.0 ± 1.4	133.1 ± 3.0	4.9 ± 0.2	37.4 ± 1.6	180.3 ± 6.5	4.8 ± 0.2
Pb//Cu-1h	20.0 ± 1.1	135.6 ± 4.3	6.8 ± 0.2	29.1 ± 1.2	194.6 ± 6.0	6.7 ± 0.2
Pb//Cu-24h	22.5 ± 1.4	139.6 ± 5.9	6.2 ± 0.3	32.6 ± 1.2	202.9 ± 7.2	6.2 ± 0.3
Cr vs Pb	Ferrihydrite			Fe(OH)OL2		
	Cr	Pb	Pb/Cr	Cr	Pb	Pb/Cr
Cr//Pb-24h	111.5 ± 3.9	116.7 ± 4.2	1.1 ± 0.1	84.6 ± 3.3	137.1 ± 4.2	1.6 ± 0.1
Cr//Pb-1h	106.0 ± 3.8	111.2 ± 4.0	1.1 ± 0.1	80.3 ± 3.9	130.9 ± 5.2	1.6 ± 0.1
Cr-Pb	100.3 ± 2.9	119.9 ± 3.5	1.2 ± 0.1	71.7 ± 2.8	144.6 ± 4.3	2.0 ± 0.1
Pb//Cr-1h	99.3 ± 3.1	123.9 ± 4.0	1.3 ± 0.1	64.6 ± 2.5	170.0 ± 5.0	2.6 ± 0.1
Pb//Cr-24h	105.0 ± 3.4	130.9 ± 3.8	1.3 ± 0.1	69.1 ± 2.8	181.1 ± 4.9	2.6 ± 0.1

3.2.7 Competitive Sorption in ternary systems

Competitive sorption studies were also carried out by adding Pb, Cr and Cu contemporaneously on ferrihydrite and Fe(OH)OL2 at pH 4.5 (Table 10). When equimolar amounts of each metal were added (100 or 200 mmol kg^{-1}; initial Pb:Cr:Cu

molar ratio of 1:1:1 or 2:2:2), the surfaces of ferrihydrite and Fe(OH)OL2 were covered with more than 50% (53-56%) by Pb, with 32-36% by Cr and with 9-13% by Cu. Covelo et al. (2004) also showed the similar behavior when these metals competed for sorption sites of four different humic umbrisols.

By adding an initial concentration of Cu twice higher than that of Pb and Cr (Pb:Cr:Cu molar ratio of 1:1:2), the sorption of Cu only slightly increased from 11 to 16% on ferrihydrite and from 13 to 20% on Fe(OH)OL2, whereas that of Pb and Cr slightly decreased. On the contrary, by increasing twice the initial concentration of Pb (Pb:Cr:Cu molar ratio of 2:1:1), the sites occupied by Pb increased substantially to 73% on ferrihydrite and 70% on Fe(OH)OL2.

Only when the initial concentration of Cr was twice greater than that of Pb and Cu (Pb:Cr:Cu molar ratio of 1:2:1), more Cr was retained than Pb on the sorbents, but the final rf values of Cr/Pb were much lower than the rf values of Pb/Cr found when the initial Pb concentration was twice greater than that of Cr and Cu (Pb:Cr:Cu molar ratio of 2:1:1). These results indicated that many sites on both sorbents were specific for both Cr and Pb, but with a higher affinity for the latter than for the former. Only when the concentration of Cr was much higher than that of Pb, larger proportion of the sorption sites could be occupied by Cr versus Pb.

Finally, it was worth mentioning that in the presence of large amounts of Pb and Cr (Pb:Cr:Cu molar of 2:1:1, 1:2:1 or 2:2:1), some sites were still occupied by Cu even though Cu had a much lower affinity than the other two metals for both the sorbents. These results indicated that small proportion of the sites on both sorbents had a high affinity for Cu, confirming the findings obtained in binary systems. Furthermore, the final Cr/Cu and Pb/Cu sorbed molar ratios were lower on Fe(OH)OL2 compared to that on ferrihydrite, substantiating that Cu competed with Cr and Pb more on Fe(OH)OL2 than on ferrihydrite, which could be ascribed to the formation of strong complexes between Cu and the organic ligands presented on organomineral complexes (Senesi and Loffredo, 2008).

Table 10 Cu, Cr and Pb in ternary systems: Sorption amounts and sorption proportions on ferrihydrite and Fe(OH)OL2

Sorbents	Pb:Cr:Cu	Sorption amounts ($\times 10^{-3}$ μmol m^{-2})			Sorption proportion (%)			Final sorption ratio (rf*)		
		Pb	Cr	Cu	Pb	Cr	Cu	Cr/Cu	Pb/Cu	Pb/ Cr
Ferrihydrite	1:1:1	105.3 ± 3.4	70.3 ± 2.8	22.0 ± 1.1	53 ± 1.8	36 ± 1.5	11 ± 0.6	3.2 ± 0.1	4.8 ± 0.2	1.5 ± 0.1
	1:1:2	101.2 ± 4.0	66.9 ± 2.5	31.7 ± 1.4	50 ± 1.9	34 ± 1.3	16 ± 0.8	2.1 ± 0.1	3.2 ± 0.1	1.5 ± 0.1
	1:2:1	96.8 ± 3.2	139.9 ± 5.2	18.7 ± 0.8	38 ± 1.3	55 ± 2.1	7 ± 2.4	7.5 ± 0.2	5.2 ± 0.2	0.7 ± 0.04
	2:1:1	177.6 ± 5.5	50.6 ± 1.7	15.2 ± 0.7	73 ± 2.2	21 ± 0.7	6 ± 2.3	3.3 ± 0.1	11.7 ± 0.3	3.5 ± 0.1
	2:2:2	145.6 ± 6.8	89.0 ± 3.1	24.2 ± 0.9	56 ± 2.4	35 ± 1.2	9 ± 0.4	3.7 ± 0.1	6.0 ± 0.3	1.6 ± 0.2
Fe(OH)OL2	1:1:1	131.7 ± 3.9	78.0 ± 2.6	31.7 ± 1.2	55 ± 1.5	32 ± 1.0	13 ± 0.5	2.5 ± 0.1	4.2 ± 0.2	1.7 ± 0.1
	1:1:2	125.7 ± 3.6	77.1 ± 2.8	50.3 ± 2.0	50 ± 1.6	30 ± 0.8	20 ± 0.7	1.5 ± 0.1	2.5 ± 0.1	1.6 ± 0.1
	1:2:1	119.4 ± 3.5	159.4 ± 5.6	29.4 ± 0.9	39 ± 1.4	52 ± 1.5	9 ± 0.4	5.4 ± 0.2	4.1 ± 0.2	0.8 ± 0.06
	2:1:1	214.0 ± 7.9	67.1 ± 2.3	25.1 ±1.0	70 ± 2.3	22 ± 0.7	8 ± 0.3	2.7 ± 0.1	8.5 ± 0.3	3.2 ± 0.1
	2:2:2	163.7 ± 4.9	103.7 ± 3.6	37.7 ± 1.1	54 ± 2.3	34 ± 0.9	12 ± 0.5	2.8 ± 0.1	4.3 ± 0.2	1.6 ± 0.1

*rf stands for the final sorbed molar ratio of Cr/Cu, Pb/Cu and Pb/ Cr

3.3 Discussions

The affinity of the heavy metals for ferrihydrite and organomineral complexes followed the sequence of Pb > Cr > Cu, as indicated by sorption isotherms, pH_{50} values, and competition in sorption in binary and ternary systems. The same sequence has been reported for the sorption of the heavy metals onto clinoptilolite (Inglezakis et al., 2003), but a sequence of Cr > Cu > Pb has been found for the sorption by Na-montmorillonite (Abollino et al., 2003). The properties of a heavy metal that affect its affinity for a sorbent include polarizability, ionization potentials, electronegativity, hydrolysis constants, ionic radious (or the radious of the hydrated ion) and softness (Gomes et al., 2001). In the present study the higher selectivity of Pb and Cr than Cu could be due, at least in part, to the higher first hydrolysis constant of the formers [Cr($10^{-4.0}$) > Pb($10^{-7.7}$) > Cu($10^{-8.0}$)] (Smith and Martell, 1976), the preference of Pb over Cr could be ascribed to the greater electronegativity of Pb [Pb(2.33) > Cu(1.90) > Cr(1.66)]. However, the sorption affinity of heavy metals on a sorbent is usually not predictable, probably because the observed results are often the effect of many factors, such as properties of the mineral, ambient conditions, metal speciation and complexing, which vary from one system to another.

3.4 Conclusions

Ferrihydrite sorbed much larger amounts of Cu, Cr and Pb than the organomineral complexes when mmol kg^{-1} mass scale was considered, owing to the larger surface area of ferrihydrite, whereas the opposite trend was true when μmol m^{-2} surface scale was taken into account. Higher organic carbon content in the precipitates induced larger sorption (μmol m^{-2}) of heavy metals. Moreover, heavy metals were sorbed stronger on organomineral complexes than that on ferrihydrite since the presence of organic ligands which provided strong complexing sites and less positive surfaces.

The competition in sorption of the heavy metals was affected by the nature and the initial concentration of the elements, the surface properties of the sorbents, the addition sequence of the trace elements and the residence time. In binary systems the

highest inhibition capacity on all the sorbents was for Pb versus Cu, whereas the lowest was for Cu versus Pb. The inhibition of Cr for Cu was much stronger than Cu for Cr. However, Cu competed with Cr and Pb more intensely on the organomineral complexes than on ferrihydrite, whereas Pb competed with Cr more intensely onto ferrihydrite. The amounts of a selected metal to be sorbed in the presence of a competing cation were greater when it was introduced earlier than when added either together with or after the other metal.

In ternary systems, when equimolar amounts of each metal were added, the surface of the sorbents were covered with more than 50% by Pb (from 53 to 56%), with 32 to 36% by Cr and with 9 to 13 % by Cu. However, even large amounts of Pb and/or Cr did not completely prevent the sorption of Cu, clearly because some sites on the sorbents had a high affinity for this metal. Only when the concentration of Cr was much higher than that of Pb, more sorption sites were occupied by Cr against Pb in binary and ternary systems.

The findings reported in this work are significant contribution to further our understanding about the factors which may affect competition in sorption of heavy metals on soil components and their mobility in soil- and sediment-water environments.

4. Biosorption of Cu, Cr and Pb on *Bacillus thuringiensis*: Competition and the Effect of Low Molecular Weight Organic Ligands

4.1 Materials and methods

4.1.1 Preparation of chemical reagent solution

Deionized distilled (DD) water was used to prepare all the solutions in present study. Stock solution of each heavy metal and anionic ligand was prepared by dissolving $Pb(NO_3)_2$, $Cu(NO_3)_2 \cdot 3H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$ and $C_6H_5Na_3O_7 \cdot 2H_2O$ (citrate), $C_2Na_2O_4$ (oxalate), $C_4H_4KNaO_6 \cdot 4H_2O$ (tartrate) in DD water, respectively. Potassium nitrate (0.02 mol L^{-1}) was used as supporting electrolyte for all experiments. The chemicals used were all analytical grade. The pH of stock solution, anionic ligands and supporting electrolyte was all adjusted to 4.5 during their preparation by 0.1 or 0.01 mol L^{-1} HNO_3 or KOH.

4.1.2 Preparation of bacterial biomass

The *B. thuringiensis* strain used in the present study was the same with Cai et al. (2009). The cells were cultured at 28 °C in sterilized beef-extracted peptone medium. After incubation in 5 ml of the medium for 7 h, 2 ml of the preculture was transferred to 200 ml of the fresh medium to grow for another 18 h. Cells were harvested and then washed thrice with DD water by centrifugation at 10,000 *g* for 10 min. Living cells were prepared by resuspending the final washed biomass with a certain volume of 0.02 mol L^{-1} KNO_3. Nonliving cells were prepared by autoclaving the resuspended living cell in DD water at 121 °C for 30 min. After centrifugation and washing by DD water again, nonliving cells were also resuspended by a certain volume of 0.02 mol L^{-1} KNO_3. The pH of both kinds bacterial suspension was adjusted to 4.5 by 0.1 or 0.01 mol L^{-1} HNO_3 or KOH. Biomass concentration in both kinds of suspension was determined by drying an aliquot volume at 60 °C to a constant weight (Puranik and Paknikar, 1999).

4.1.3 Sorption of heavy metals

Preliminary experiments revealed that 2 h was enough for three heavy metals to attain the sorption equilibrium on both living and nonliving cells. Sorption isotherm was observed by mixing suitable volume of prepared bacterial suspension which contained 4 mg cells with different concentration of heavy metal in 0.02 mol L^{-1} KNO_3 in a series of centrifuge tubes, the total volume of the mixture was 8 ml. The mixture was shaken at 25 °C for 4 h and the pH of each sample was kept constant at 4.5 by 0.1 mol L^{-1} KOH or HNO_3. The final suspension was centrifuged at 10,000 *g* for 20 min. Heavy metal amount in the supernatant was determined by atomic absorption spectrometry (Varian AAS240FS). The sorption of heavy metal was calculated by subtracting the amount in supernatant from that initially added. Similarly, competitive sorption of three heavy metals in ternary system was studied by adding equal amount of each metal simultaneously. Sorption experiments of 0.5 mmol L^{-1} individual heavy metal on 4.0 mg bacteria were also conducted in the presence of anionic ligand with increasing the molar ratio of ligand to heavy metal ($R_{L/M}$) from 0.5 to 3.0 in 8 ml solution.

4.1.4 Desorption of sorbed heavy metals

Four micromole of each heavy metal was mixed with 4.0 mg of living or nonliving cells in 8 ml solution. The mixture was shaken at 25 °C with constant pH of 4.5 for 4 h and centrifuged at 10,000 *g* for 20 min. The final residue (heavy metal-bacteria complex) was resuspended by 8 ml of 0.1 mol L^{-1} EDTA. After shaking at 25 °C for 4 h, the desorbed heavy metals were collected by centrifugation again and determined by atomic absorption spectrometry.

Both sorption and desorption experiments in current study were performed in triplicate and the relative standard deviation was lower than 5%.

4.2 Results

4.2.1 Sorption isotherms

Sorption isotherms of Pb, Cu and Cr in single system on living and nonliving *B. thuringiensis* are displayed in Fig.9. The data was fitted by Langmuir equation and

Freundlich equation, respectively. The Langmuir equation could be expressed as $X = X_m KC/(1+KC)$, where C and X are the amount of examined heavy metal in the solution (mmol L^{-1}) and sorbed on the sorbent (mmol kg^{-1}), respectively, X_m stands for the maximum amount of heavy metal that may be sorbed and K is a constant related to the sorption energy. The empirical expression of Freundlich equation was: $q_e = K_f C_e^{1/n}$, where C_e and q_e have the same indicating function with C and X in Langmuir equation, while K_f and n is the indicating constant of sorption capacity and sorption intensity, respectively.

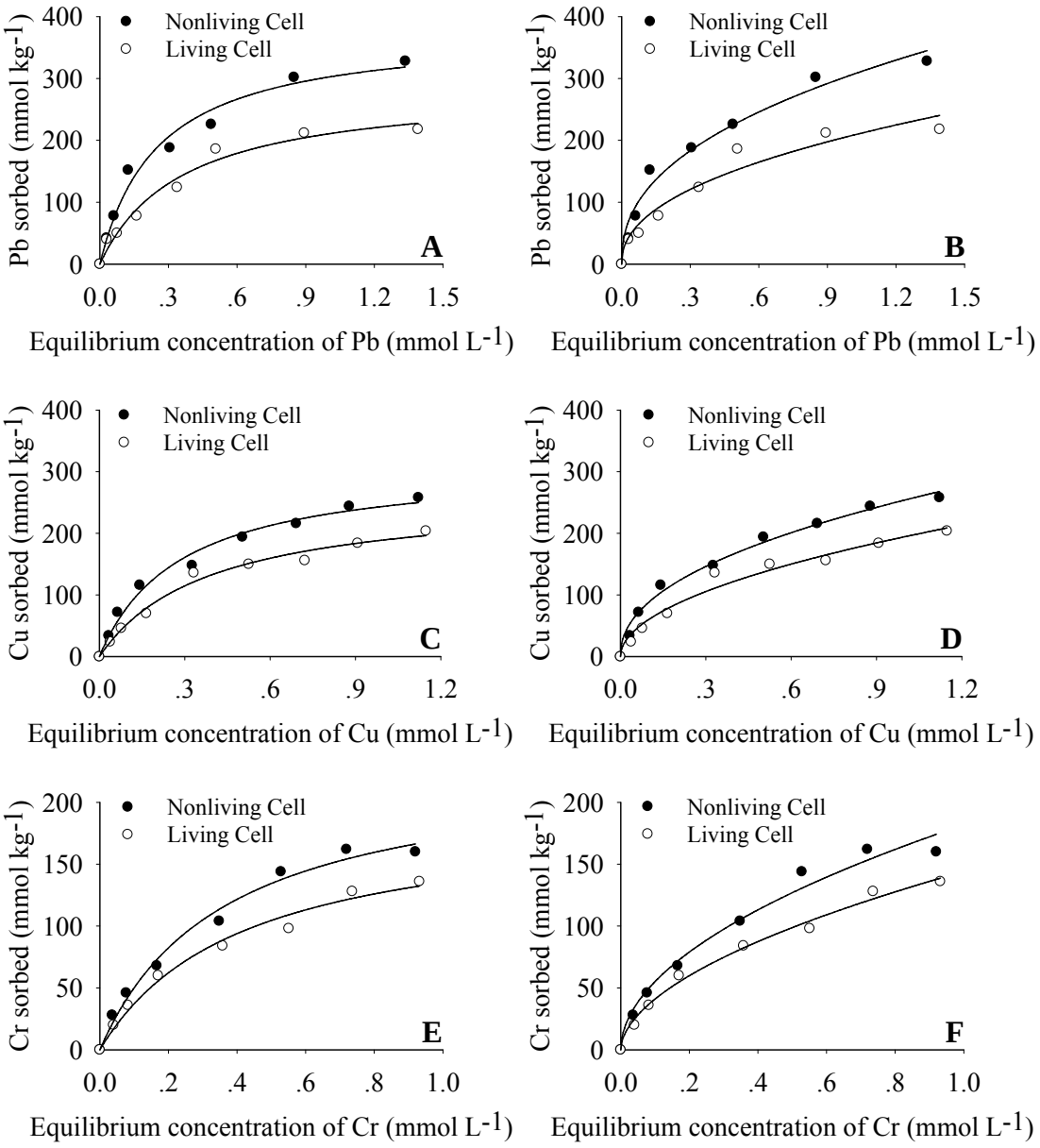

Fig.9. Langmuir (A, C, E) and Freundlich (B, D, F) fitting for the sorption isotherms of Pb, Cu and Cr on living and nonliving *B. thuringiensis*

Table11 Isotherm parameters for the sorption of Pb, Cu and Cr on living and nonliving *B. thuringiensis*

Metal	Cells	Langmuir fitting			Freundlich fitting		
		X_m (mmol kg^{-1})	K	R^2	K_f(mmol kg^{-1})	n	R^2
Pb	Living cell	286.4	2.78	0.97	207.2	2.23	0.95
	Nonliving cell	378.7	3.96	0.98	305.1	2.36	0.97
Cu	Living cell	262.4	2.59	0.98	194.6	1.97	0.97
	Nonliving cell	313.1	3.52	0.98	254.2	2.18	0.98
Cr	Living cell	191.2	2.41	0.98	144.1	1.83	0.98
	Nonliving cell	231.9	2.76	0.98	181.8	1.93	0.98

As reported in Table 11, the sorption isotherms can be described by either Langmuir equation or Freundlich equation, the fittings by former equation were often better than that by the latter. The maximum sorption of Pb, Cu and Cr on living cells from Langmuir fitting was 286.4, 262.4 and 191.2 mmol kg^{-1} while that on nonliving cells was 378.7, 313.1 and 231.9 mmol kg^{-1}, respectively. The K values of examined heavy metals for nonliving cells were all higher than that for living cells. These results indicated that both sorption capacity and affinity of examined heavy metals were greater on nonliving cells than that on living cells and followed the sequence of Pb > Cu > Cr on both cells. The same trends could be found by comparing the parameters that derived from the fitting of Freundlich equation.

4.2.2 Competitive sorption in ternary system

Sorption isotherms of Pb, Cu and Cr in ternary system on living and nonliving *B. thuringiensis* are presented in Fig.10. The application of Langmuir equation was satisfied in fitting the sorption of Pb and Cu (R^2 > 0.92) but was unsatisfied in the case of Cr on both cells. With the increasing of heavy metal concentration in the examined range, the sorption of Pb was increased at all while that of Cr was increased just in the initial stage and then declined after a peak and leveled off finally. It was

clear that the competitive ability of examined heavy metals on both cells followed the order of Pb > Cu > Cr, which was in agreement with their sorption affinity in single system. Compared to single system, the sorption of Pb and Cu was decreased by 37% and 57% on living cells while by 28% and 43% on nonliving cells (Table 12), sorption amount of Cr was also less on living cells than that on nonliving cells. These results suggested that the competition among examined heavy metals for the sorption sites was stronger on living cells than that on nonliving cells.

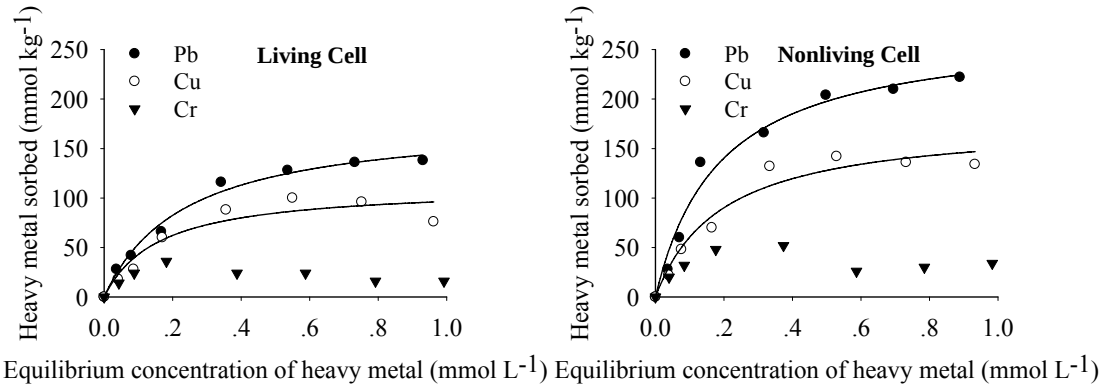

Fig.10. Sorption isotherms of Pb, Cu and Cr in ternary system on living and nonliving *B. thuringiensis*

Table12 Isotherm parameters for the sorption of Pb, Cu and Cr in ternary system on living and nonliving *B. thuringiensis*

Metal	Living cell				Nonliving cell			
	X_m (mmol kg^{-1})	K	R^2	*IE	X_m (mmol kg^{-1})	K	R^2	*IE
Pb	179.6	4.24	0.98	37%	271.7	5.34	0.97	28%
Cu	112.0	6.24	0.92	57%	177.3	5.17	0.96	43%
Cr	----	----	----	----	----	----	----	----

*IE stands for the inhibitive efficiency of a metal by the other two metals and was calculated by comparing the sorption capacity of the metal in ternary system to that in single system

4.2.3 Effect of citrate, oxalate and tartrate on the sorption

The effects of citrate, oxalate and tartrate on the sorption of Pb, Cu and Cr by

living and nonliving *B. thuringiensis* are illustrated in Fig.11. The sorptions of examined heavy metals were inhibited by the presence of anionic ligands. In order to evaluate the inhibitive effect of examined ligands, the inhibitive efficiency was calculated according to the following expression: Inhibitive efficiency of ligand (%) = (1 - heavy metal sorption in the presence of ligand / heavy metal sorption in the absence of ligand) ×100. With increasing the ratio of ligand to heavy metal ($R_{L/M}$) from 0.5 to 3.0 by keeping the constant amount of heavy metal and increasing the concentration of anionic ligand, the inhibitive efficiency of citrate, oxalate and tartrate on heavy metal sorption by living cells increased from 22 to 57, 20 to 43 and 12 to 33% for Pb, from 35 to 63, 24 to 49 and 17 to 40% for Cu, from 19 to 43, 12 to 38 and 14 to 30% for Cr, respectively. The efficiency of citrate, oxalate and tartrate in reducing heavy metal sorption on nonliving cells was 28-58, 20-47 and 18-42% for Pb, 33-69, 31-60 and 25-46% for Cu, 22-50, 17-49 and 11-36% for Cr, respectively. These results revealed that the ability of anionic ligands in depressing heavy metal sorption on both living and nonliving cells followed the order of citrate > oxalate > tartrate and more heavy metals was inhibited by anionic ligands for being sorbed on nonliving cells than that on living bacteria.

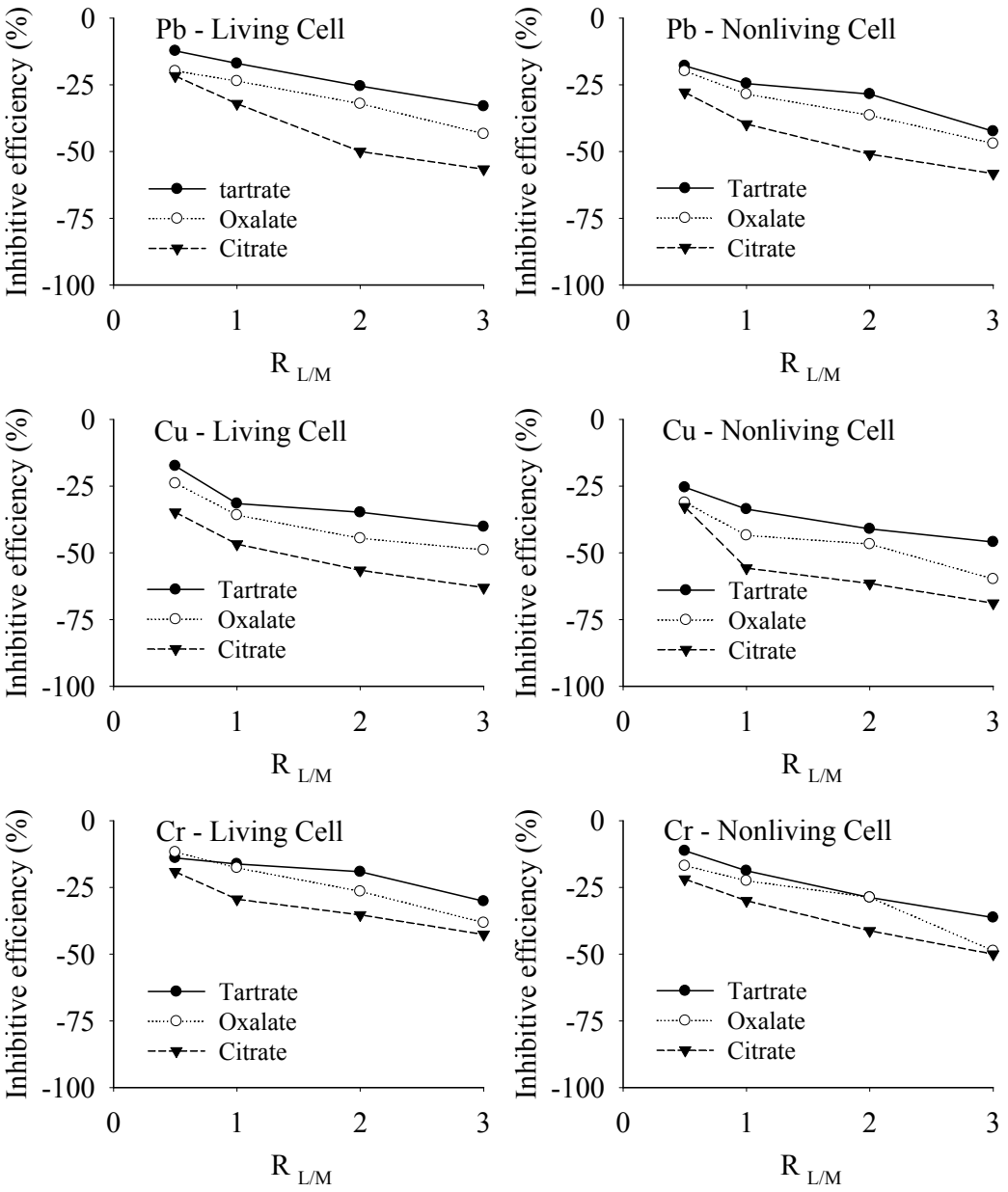

Fig.11. Inhibitive efficiency of citrate, oxalate and tartrate on the sorption of Pb, Cu and Cr by living and nonliving *B. thuringiensis*

4.2.4 Desorption

As shown in Fig.12, the desorption percentage of Pb, Cu and Cr by EDTA from living *B. thuringiensis* was 81, 84 and 77% while that from nonliving cells was 83, 88 and 80%, respectively, suggesting little differences between desorption percentages by EDTA from living cells and that from nonliving cells. Our preliminary experiments also revealed that the sorption of examined heavy metals on both living and nonliving cells attained the equilibrium within a short time (2 h) (data not show).

These results may suggest that active uptake took up little part in the sorption of heavy metals by living cells. The affinities of binding sites on the cell wall for heavy metals are unlikely greater than that of EDTA (Shuttleworth and Unz, 1993), the molecular size of EDTA is relative larger, nonextractable metals by EDTA may be ascribed to the diffusion of heavy metals into the porous structure of the cell surface and then became inaccessible to EDTA.

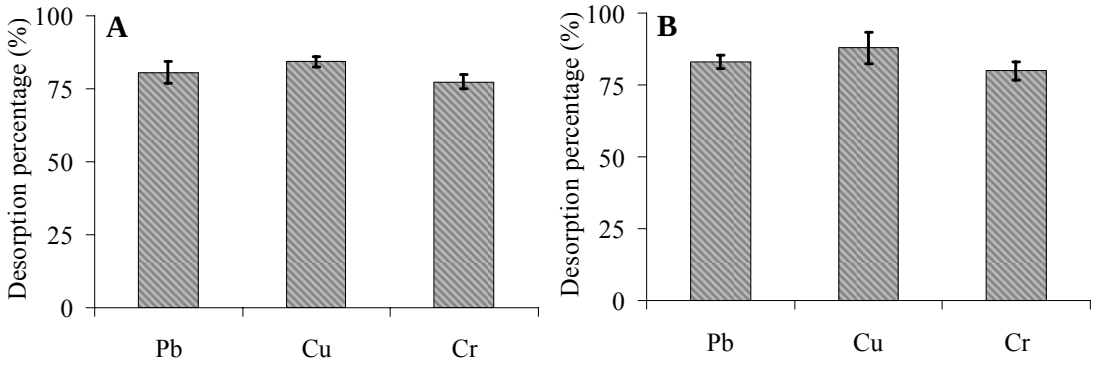

Fig.12. Desorption percentage of Pb, Cu and Cr by EDTA from living (A) and nonliving (B) *B. thuringiensis*

4.3 Discussions

Higher capacity and greater affinity of heavy metal sorption on nonliving *B. thuringiensis* than that on living cells were observed in present study. Higher sorption capacity of nonliving bacteria than that of living cell for heavy metals has also been found by Gabr et al. (2008) and Zouboulis et al. (2004). During metabolism, a membrane-induced proton motive force has been reported in investigating the binding ability of metal by living *B. subtilis* (1992). The sorption of heavy metals on living cells might be limited by the competition of these pumped protons. After heat treatment, the enzymes which controlled the active uptake on living cells might be destroyed and then resulted in the reduction of heavy metal sorption (Chen et al., 2005). However, our desorption observation (Fig.12) and kinetic result (data not show) indicated that active uptake probably take up little part in the sorption of heavy metals on living *B. thuringiensis*. Besides, Gabr et al. (2008) and Srinath et al. (2002) inferred that the cell wall of bacteria would have been broken and the latent binding

sites for metals would be exposed after thermal treatment. Therefore, the absence of competition from pumped protons and the exposure of intracellular binding sites might be the reasonable explanations for the increase of heavy metal sorption on heat treated cells compared to the living cells in current study.

The competitive ability of examined heavy metals followed the order of Pb > Cu > Cr on both cells and stronger competition was observed on living cells than that on nonliving cells in present study. Although some literatures reported that the stability constant of metal-carboxyl and metal-phosphate complexes on bacterial cell wall was slightly higher for Cu than that for Pb (Table 2) (Fein et al., 1997; Daughney et al., 1998; Ngwenya et al., 2003), our observation and some other studies showed that the competitive ability or sorption affinity of Pb on bacteria was greater than that of Cu (Puranik and Paknikar, 1999; Pagnanelli et al., 2003; Tunali et al., 2006). This disaccord may indicate the participation of other functional groups such as amido and hydroxyl in the sorption. Hydroxyl and/or amido have already been found to be important candidates in the sorption of Pb by *Bacillus cereus* and the sorption of Cu by *Arthrobacter nicotianae* (Nakajima, 2002; Pan et al., 2006). Trivalent Cr was less competent than bivalent Pb and Cu in competitive sorption, one possible explanation was that the species of Cr^{3+}, $Cr(OH)^{2+}$ and $Cr(OH)_2^{+}$ were coexistent while $Cr(OH)^{2+}$ was the dominated species at pH 4.5 (the pH observed in current study) (Adriano, 2001). Actually, several intrinsic indexes such as first hydrolysis constant, electronegativity, ionic radius and softness of the heavy metals have been suggested as the potential factors that resulted in the preference in competitive sorption (Gomes et al., 2001). The selectivity of Pb > Cu > Cr in competitive sorption in our investigation was in agreement with their electronegativity [Pb(2.33) > Cu(1.90) > Cr(1.66)]. The uniformity of sorption affinity with electronegativity and ionic radius of heavy metals has also been reported previously on algal cells (Abu Al-Rub et al., 2006; Singh et al., 2007). In addition, larger first hydrolysis constant [Pb($10^{-7.7}$) > Cu($10^{-8.0}$)] and softness [Pb(3.58) > Cu(2.89)] of Pb than that of Cu were also suggested as the possible explanation for the higher affinity of Pb over Cu in the sorption by *Sphaerotilus natans* (bacterium) and soils (Misono et al., 1967; Smith and

Martell, 1976; Pagnanelli et al., 2003; Usman, 2008). The loosely held metals can be replaced easily by the other metals (Qin et al., 2006). In addition, with the same amount of free metals, the competition might be relieved by increasing the sorption sites. Weaker affinity and lower capacity of heavy metals sorption on living cells than that on nonliving cells thus accounted for the stronger competition on the former sorbent than that on the latter.

The sorption of Cu, Cr and Pb was depressed by citrate, oxalate and tartrate on both cells especially nonliving bacteria and the inhibitive ability of ligands on each metal followed the order of citrate > oxalate > tartrate. The affinity of examined heavy metals for nonliving bacteria was greater than that for living cells, accordingly, the influence of ionic strength on the heavy metal sorption should be stronger on living cells than that on nonliving cells. However, the inhibitive efficiencies of citrate, oxalate and tartrate on the sorption of heavy metals by nonliving cells was greater than that by living cells. This inconsistency may suggest that the concomitant influence of ionic strength was not important compared to the effect of anionic ligand in current study. Taking H_nL as the general formula of citric acid, oxalic acid and tartaric acid, Cu could form complex of CuH_2L with citrate while of CuHL, CuL, CuL_2 with oxalate and CuL, CuL_2, CuL_3, CuL_4 with tartrate in present study (pH4.5) by considering their dissociation constant (p*K*a) (Table 4) (Glover II et al., 2002; Wuhan University, 2004; Yuan et al., 2007). The greatest stability constants (log*K*s) of these corresponding Cu-ligand complexes listed in Table 4 generally followed the order of citrate > oxalate > tartrate and were higher than most reported stability constants of Cu with carboxyl and phosphate on bacterial surface (Table 3) (Fein et al., 1997; Daughney et al., 1998; Ngwenya et al., 2003; Fang et al., 2009). The log*K*s values related to Cr are generally unknown, the log*K*s values related to Pb followed the same trend with Cu. These coincidences probably suggest that greater stability constants of heavy metal with free ligands than that with functional groups on bacterial surface was the driven force for the inhibitive effect of examined ligands on the biosorption of heavy metals. Similar hypothesis has been proposed by Shuttleworth and Unz (1993). The following formation of less positive, neutral or

negative charged complexes of heavy metals with free ligands reduced the sorption of heavy metals by living and nonliving bacteria. With the same dosage of initial addition, less amounts of free heavy metals were required to attain the sorption equilibrium on living cells than that on nonliving cells since the lower capacity of former sorbent than the latter in retaining heavy metals. The resistance of heavy metal sorption to the decrease of free heavy metals thus might be greater on living cells than that on nonliving cells. Greater resistance to the decrease of free heavy metals thereby accounted at least in part for the weaker inhibition of free ligands on the sorption of heavy metals by living cells, the nutritional uptake or degradation of ligands by living cells were also the possible explanation.

Table13 Formula, dissociation constant (p*K*a) of organic acid (H_nL) and stability constant (log*K*s) of metal-ligand complex (Glover II et al., 2002; Wuhan University, 2004; Yuan et al., 2007).

Acid	Formula	pK_a	log*K*s		
			Cu	Pb	Cr
Citric acid	CH_2-COOH $HO-C-COOH$ CH_2-COOH	pKa_1 = 3.13 pKa_2 = 4.76 pKa_3 = 6.40	Log(CuH_2L) = 12.0 Log(CuHL) = 6.1 Log(CuL) = 18.0	Log(PbH_2L) = 11.2 Log(PbHL) = 5.2 Log(PbL) = 12.3	
Oxalic acid	COOH | COOH	pKa_1 = 1.22 pKa_2 = 4.19	Log(CuHL) = 6.25 Log(CuL) = 4.5 Log(CuL_2) = 8.9	Log(PbL) = 4.2 Log(PbL_2) = 6.3	
Tartaric acid	HO—CH—COOH | HO—CH—COOH	pKa_1 = 3.04 pKa_2 = 4.37	Log(CuL) = 3.2 Log(CuL_2) = 5.11 Log(CuL_3) = 4.78 Log(CuL_4) = 6.51	Log(PbL) = 3.78 Log(PbL_3) = 4.7	

4.4 Conclusions

Our results suggested that the sorption of Pb, Cu and Cr by *B. thuringiensis* was greater and stronger on nonliving cells than that on living cells. The competition among three heavy metals in the sorption was more intensive on living cells than that on nonliving counterparts and the competitive ability followed the order of Pb > Cu > Cr on both cells. The sorption of examined heavy metals was depressed by anionic ligands especially on nonliving bacteria, a sequence of citrate > oxalate > tartrate in inhibitive ability was observed on both cells. These results are of significant importance for the evaluation or remediation of soil heavy metal pollution.

5. Competitive Sorption of Cu and Cr on Goethite and Goethite-bacteria Complex

5.1 Materials and methods

5.1.1 Preparation of chemical reagent solution

The chemicals used in the present study were all analytical grade. Deionized distilled (DD) water was used to prepare all the solutions. Stock solution of each heavy metal was prepared by dissolving $Cu(NO_3)_2 \cdot 3H_2O$ and $Cr(NO_3)_3 \cdot 9H_2O$ in DD water, respectively. Potassium nitrate (0.02 mol L^{-1}) was prepared as supporting electrolyte for all experiments. The pH of stock solution and supporting electrolyte was adjusted to 4.5 by 0.1 or 0.01 mol L^{-1} HNO_3 or KOH.

5.1.2 Synthesis and characterization of goethite

Goethite was synthesized according to Atkinson et al. (1967). Fifty gram of $Fe(NO_3)_3 \cdot 9H_2O$ in 825 ml of deionized water was precipitated by the slow addition of 200 ml of 2.5 mol L^{-1} NaOH under vigorous stirring. After six days of aging at 60 °C, the precipitate was dialyzed, air-dried and then ground to pass a 100 mesh sieve. The final product was identified as goethite by X-ray diffraction (data not shown). The specific surface area and PZC of goethite was 96.4 m^2 g^{-1} and 8.3 as measured by high speed automated surface area and pore size analyzer (Quantachrome Autosorb-1, USA) and Mehlich method (Xiong, 1985), respectively.

5.1.3 Preparation of bacteria

Untreated biomass of *B. thuringiensis* was prepared according to *4.1.2.*

5.1.4 Preparation of goethite-bacteria complex

Four gram of goethite was suspended with 195 ml of 0.02 mol L^{-1} KNO_3 in conical flask, the pH was adjusted to 4.5 by adding 0.1 or 0.01 mol L^{-1} HNO_3 or KOH until equilibrium. The final volume of the suspension was adjusted to 200 ml by adding suitable volume of 0.02 mol L^{-1} KNO_3. Preliminary experiment was carried

out to investigate the sorption of *B. thuringiensis* on goethite as described by Rong et al. (2010). In a batch of centrifuge tubes, 2 ml of goethite stock suspension (20 mg ml^{-1}, pH 4.5) was mixed with different volumes of bacterial suspension to construct sorption isotherm, supplemental volumes of 0.02 mol L^{-1} KNO_3 (pH 4.5) was added to make the total volume of each mixture was 8 ml. The mixtures were shaken at 25°C for 1 h. After the addition of 1 ml sucrose solution (60% by weight), unattached bacteria in the mixture was collected by centrifugation at 10,000 *g* for 20 min. The final residue was goethite-bacteria complex. The amount of bacteria in the supernatant was determined directly by spectrophotometry, the sorption amount of bacteria was calculated by subtracting the quality of bacteria in the supernatant from that added initially. The experiment showed that sorption isotherm of *B. thuringiensis* on goethite was H-type (Sparks, 2002). A constant amount (43.6 ± 0.1 mg) of goethite-*B. thuringiensis* complex was prepared for the following experiments, the sorption of bacteria in the complex was saturated.

5.1.5 Sorption kinetics and isotherms of Cu and Cr in single and binary systems

Goethite-*B. thuringiensis* complex prepared as described in *2.4* was resuspended by a certain volume of 0.02 mol L^{-1} KNO_3 (pH 4.5) and mixed with 4 μmol of $Cu(NO_3)_2$ and $Cr(NO_3)_3$ individually (single system) or together (binary system). The total volume of the mixture was 8 ml. The mixtures were shaken at 25 °C for different time period from 0.083 to 24 h to investigate the sorption kinetics. Batch experiments were also carried out by mixing the same mass of goethite-*B. thuringiensis* complex with different amount of $Cu(NO_3)_2$ or $Cr(NO_3)_3$ individually (single system) or together (binary system; the initial molar ratio of Cu to Cr was 1) in 8 ml supporting electrolyte solution. The mixtures were shaken at 25 °C for 24 h to construct the sorption isotherms. The pH of each sample was kept at 4.5 by 0.1 mol L^{-1} KOH or HNO_3. After centrifugation at 10,000 *g* for 20 min, the amount of heavy metal in each supernatant was determined by atomic absorption spectrometry (Varian AAS240FS). The sorption of each heavy metal was then calculated by the difference between the amount of the metal introduced initially and that remained in the supernatant. Similar

experiments were also carried out on the same amount of pure goethite for comparison.

5.1.6 Desorption of sorbed Cu and Cr

Goethite-*B. thuringiensis* complex prepared as described in *2.4* was resuspended by a certain volume of 0.02 mol L^{-1} KNO_3 (pH 4.5) and mixed with 4 μmol of $Cu(NO_3)_2$ and $Cr(NO_3)_3$ individually (single system) or together (binary system). The same experiments were carried on the same mass of pure goethite in 8 ml of total mixture volume. The mixtures were shaken at 25 °C at pH 4.5 for 24 h. After centrifugation at 10,000 *g* for 20 min, the supernatants and the residues were collected separately, the heavy metal-sorbent complex was washed by DD water and then resuspended by 8 ml of 0.1 mol L^{-1} $Ca(NO_3)_2$. After shaking at 25 °C at pH 4.5 for 8 h, the desorbed heavy metals were collected and determined as described previously.

All the sorption and desorption experiments were conducted in triplicate and the relative standard deviations were lower than 4%.

5.2 Results

5.2.1 Sorption kinetics of Cu and Cr in single and binary systems

Sorption kinetic curves of Cu and Cr in single and binary systems on goethite and goethite-*B. thuringiensis* complex are depicted in Fig.13. The kinetic data were fitted by several kinetic models. The fittings were best by the pseudo-second-order model, which has been applied widely and satisfactorily in the sorption of heavy metals on various sorbents (Ho and Mckay, 2000; Ho, 2003; Qin et al., 2006; Chen and Li, 2010). The linear form of the pseudo-second-order model can be expressed as:

$$t/q_t = 1/(kq_e^2)+t/(q_e)$$

$$h = kq_e^2$$

where q_t and q_e are the amounts of heavy metal sorbed at time t and at equilibrium (mmol kg^{-1}), k is the rate constant of sorption (kg $mmol^{-1}$ h^{-1}) and h is the initial sorption rate (mmol kg^{-1} h^{-1}) (Ho and Mckay, 2000).

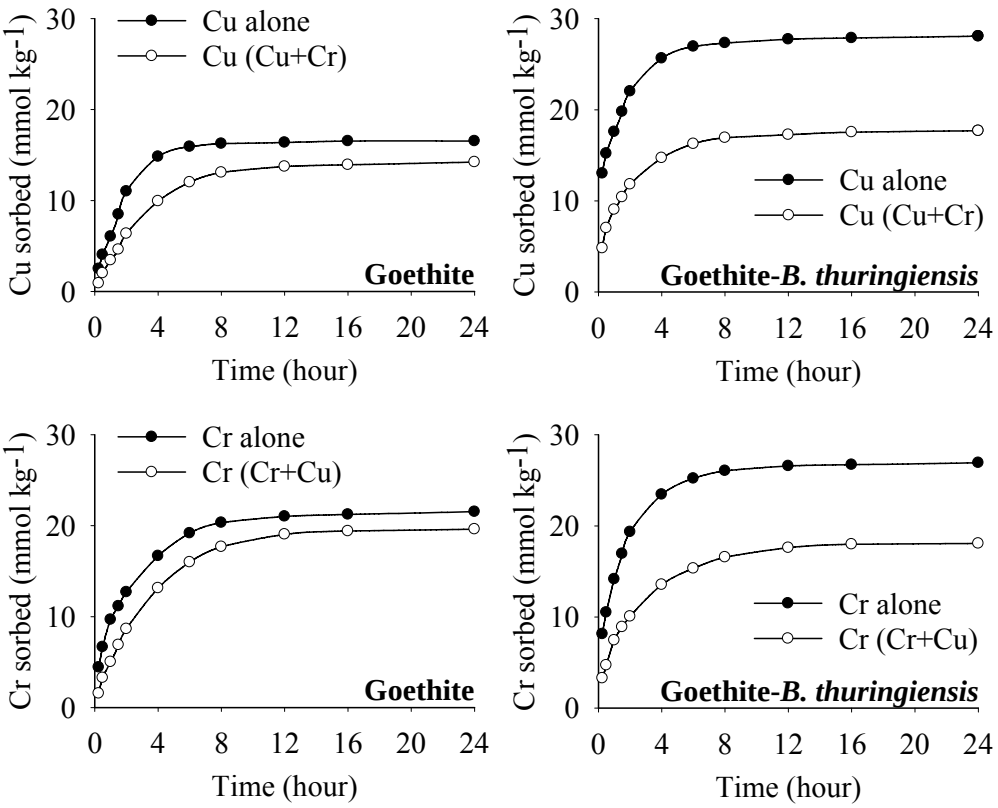

Fig.13. Sorption kinetics of Cu and Cr in single and binary systems by goethite and goethite-bacteria complex

The kinetic parameters are listed in Table 14. All the correlation coefficients (R^2) were higher than 0.990, indicating very good description of the experimental data by Pseudo-second-order model. In single systems, the initial sorption rate (*h*) of Cu was slower than that of Cr on goethite (13.44 mmol kg^{-1} h^{-1} vs 17.61 mmol kg^{-1} h^{-1}) while the opposite was true on goethite-*B. thuringiensis* complex (58.16 mmol kg^{-1} h^{-1} vs 35.49 mmol kg^{-1} h^{-1}). However, the pseudo-second-order rate constant (*k*) of Cu in single systems was greater than that of Cr on both sorbents. These results suggested that the initial sorption rate of Cr was faster than that of Cu on goethite while Cu was faster than Cr in reaching sorption equilibrium (sorption rate in whole sorption process). Both initial sorption rate and sorption rate in whole sorption process of Cu on goethite-*B. thuringiensis* complex were faster than that of Cr. Faster sorption of both heavy metals on goethite-*B. thuringiensis* complex than that on pure goethite were also revealed. Table 14 also shows that both initial sorption rate and sorption rate

in whole sorption process of each heavy metal in binary systems were lower than that in single systems on both sorbents, indicating the inhibition on initial and whole sorption rate by the competition between heavy metals.

Table14 Kinetic parameters for the sorption of Cu and Cr in single and binary systems on goethite and goethite-bacteria complex by fitting Pseudo-second-order model

Sorbent	Metal	System	q_e (mmol kg^{-1})	h (mmol kg^{-1} h^{-1})	k	R^2
Goethite	Cu	Cu alone	17.83	13.44	0.0423	0.997
		Cu + Cr	16.83	4.97	0.0176	0.990
	Cr	Cr alone	22.89	17.61	0.0336	0.999
		Cr + Cu	22.78	7.50	0.0145	0.995
Goethite-*B. thuringiensis*	Cu	Cu alone	28.73	58.16	0.0705	0.999
		Cu + Cr	18.47	19.98	0.0585	0.999
	Cr	Cr alone	27.99	35.49	0.0453	0.999
		Cr + Cu	19.48	12.38	0.0326	0.999

5.2.2 Sorption isotherms of Cu and Cr in single and binary systems

The sorption isotherms of Cu and Cr in single and binary systems by goethite and goethite-*B. thuringiensis* complex are shown in Fig.14. The sorption data were fitted by Langmuir equation:

$$X = X_m KC/(1+KC)$$

where C is the concentration of heavy metal in the solution (mmol L^{-1}), X is the amount of heavy metal sorbed on the sorbent (mmol kg^{-1}), X_m stands for the maximum amount of heavy metal that may be sorbed (sorption capacity), and K is a constant related to the sorption energy. The greater the K value, the higher the affinity between the heavy metal and the sorbent (Sparks, 2002).

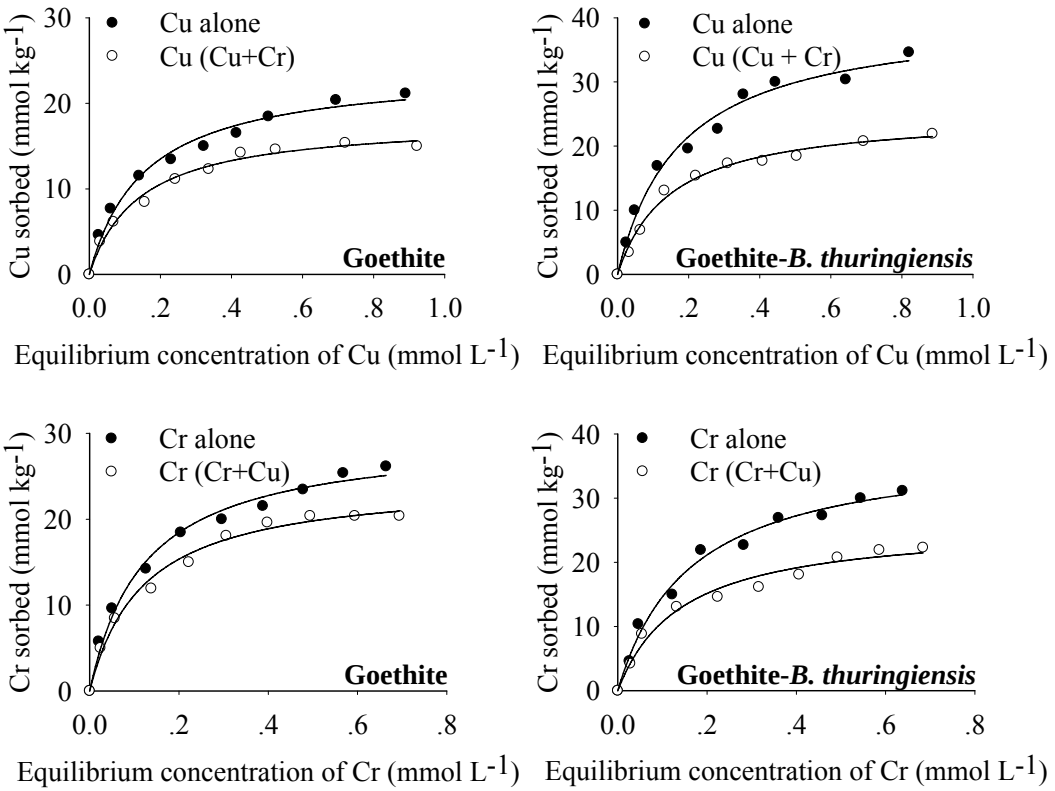

Fig.14. Sorption isotherms of Cu and Cr in single and binary systems by goethite and goethite-bacteria complex

As reported in Table 15, in single systems, the maximum sorption of Cu and Cr on goethite was 23.98 and 29.71 mmol kg^{-1} and that on goethite-*B. thuringiensis* complex was 40.51 and 38.27 mmol kg^{-1}, respectively. The *K* values of heavy metals for goethite were greater than that for goethite-*B. thuringiensis* complex and that of Cr were higher than Cu for both sorbents. These results indicated that higher capacities of heavy metals were sorbed by goethite-*B. thuringiensis* complex while the metals were sorbed more strongly by goethite. By comparing the sorption capacity of each heavy metal on goethite-*B. thuringiensis* complex with that on pure goethite, it was interesting to find that the enhancement of sorption capacity (ESC) of Cu (69%) was greater than that of Cr (29%) although pure goethite showed greater capacity for Cr than for Cu (Table 15), suggesting that the immobilized bacteria had higher sorption capacity for Cu than for Cr.

The sorption isotherms of Cu and Cr in binary systems on goethite and

goethite-*B. thuringiensis* complex can also be fitted satisfactorily by Langmuir equation ($R^2 > 0.97$) (Table 15). The total sorption of Cu and Cr in binary systems were much higher than the sorption capacity of each heavy metal in single systems on both sorbents especially goethite, indicating the heterogeneity of these heavy metals in some of their sorption sites. However, the sorption capacity of each heavy metal decreased in binary systems compared to that in single systems, suggesting the inhibition on the sorption of heavy metals by their competition for homogeneous sorption sites. By comparing the sorption in binary systems with that in single systems, the maximum sorption of Cu was reduced by 25% on goethite and by 38% on goethite-*B. thuringiensis* complex, and that of Cr was depressed by 17% and 32% on goethite and goethite-*B. thuringiensis* complex, respectively (Table 15). Greater inhibition of Cr for Cu than Cu for Cr on the sorption by both sorbents indicated higher selectivity of both sorbents for Cr than for Cu. Stronger inhibition of heavy metal sorption by the competing metal on goethite-*B. thuringiensis* complex than that on goethite suggested that the competition between Cu and Cr was more intensive on the former than on the latter sorbent.

Table15 Isotherm parameters for the sorption of Cu and Cr in single and binary systems on goethite and goethite-bacteria complex by fitting Langmuir equation

Metal	System	Goethite				Goethite-*B. thuringiensis*				*ESC
		X_m (mmol kg^{-1})	K	R^2	*IE	X_m (mmol kg^{-1})	K	R^2	*IE	
Cu	Cu alone	23.98	6.43	0.98	----	40.51	5.64	0.98	----	69%
	Cu + Cr	18.02	7.03	0.98	25%	25.09	6.72	0.99	38%	39%
Cr	Cr alone	29.71	8.18	0.98	----	38.27	6.18	0.98	----	29%
	Cr + Cu	24.56	8.33	0.98	17%	25.95	7.02	0.97	32%	6%

*IE stands for the inhibitive efficiency of a given metal by the competing metal and was calculated by comparing the sorption capacity of the given metal in binary system to that in single system;

*ESC stands for the enhancement of the sorption capacity of examined metal on Goethite-*B. thuringiensis* complex compared to that on equal mass of goethite.

5.2.3 Desorption

Desorption of Cu and Cr which were previously sorbed in single and binary systems on goethite and goethite-*B. thuringiensis* complex by 0.1 mol L^{-1} $Ca(NO_3)_2$ was conducted at pH 4.5 (Table 16). The desorption ratio of sorbed Cu from goethite-*B. thuringiensis* complex was 38.3% and 22.7% while that from goethite was 18.8% and 10.9% when the metal was sorbed in single and binary sorbate system. The percentage of Cr desorbed from goethite-*B. thuringiensis* complex was 29.0% and 18.2% when the metal was sorbed in single and binary sorbate system whereas that from goethite was less than 9.6%. These results suggested that little percentage of sorbed metals could be released by $Ca(NO_3)_2$ from goethite while higher ratio of sorbed metals could be extracted from goethite-*B. thuringiensis* complex, confirming that heavy metals were sorbed more tightly on goethite than on goethite-*B. thuringiensis* complex. Lower desorbability of heavy metals from goethite may be due to the specific sorption and/or entrapment of the metal into the cracks or defects in goethite structure (Mustafa et al., 2004; 2006). For each sorbed metal, it was observed that the desorption (percentage) usually slightly higher from single sorption systems than those from binary sorption systems, indicating the release of loosely sorbed metal and the retention of tightly bound cation during the competitive sorption.

Table16 Desorption of fixed Cu and Cr in single and binary systems by $Ca(NO_3)_2$ from goethite and goethite-bacteria complex

Sorbent	Metal	System	Sorption (mmol kg^{-1})	Desorption (mmol kg^{-1})	Desorption percentage (%)
Goethite	Cu	Cu alone	16.54	3.11	18.8
		Cu + Cr	14.23	1.55	10.9
	Cr	Cr alone	21.54	2.07	9.6
		Cr + Cu	19.62	1.41	7.2
Goethite-*B. thuringiensis*	Cu	Cu alone	28.12	10.77	38.3
		Cu + Cr	17.69	4.02	22.7
	Cr	Cr alone	26.92	7.81	29.0
		Cr + Cu	18.08	3.29	18.2

5.3 Discussions

An enhancement in sorption capacity of each heavy metal in single systems on goethite-*B. thuringiensis* complex compared to that on equal mass of goethite was observed in current study. Electrostatic attraction was considered as the primary mechanism in the interaction of positively charged iron oxide and negatively charged bacteria (Jiang et al., 2007; Rong et al., 2010). Goethite particles were attached on the surface of bacteria in goethite-bacteria complex due to the larger size of the cells compared to the iron oxides (Glasauer et al., 2001; Rong et al., 2010). However, the attachment of oxides could be disproportioned since the heterogeneous distribution of charges on the bacterial surface, the steric hindrance, the hydrophobic nature of cell wall and the hydrophilicity of iron oxides (Glasauer et al., 2001). The cell wall in goethite-*B. thuringiensis* complex in current study thus was probably not fully covered by goethite. Templeton et al. (2003) also found that goethite did not significantly block the functional groups on bacterial surface despite the strong association of goethite particle with bacteria in *Burkholderia cepacia*-goethite

composite. Sorption capacities of Cu and Cr in present study on pure bacteria were much higher than that on pure goethite. Besides, heavy metals have been found to be preferentially sorbed on the biotic fraction of bacteria-goethite composites especially at lower pH (Templeton et al., 2003), probably due to the lower pk_a values of the functional groups on bacteria surface (eg. carboxyl, phosphate) than that on goethite surface (hydroxyl) (Fein et al., 1997; Venema et al., 1998; Templeton et al., 2003). Moreover, in goethite-*B. thuringiensis* complex, the dominant positive charges on the goethite were probably reversed by the abundant anionic functional groups on the bacteria, just as anion adsorption can reverse the zeta potential of the surface of iron oxide (Erdemoğlu and Sarıkaya, 2006), thereby promoting the sorption of heavy metals on exposed goethite. Therefore, greater amounts of heavy metals were sorbed on goethite-*B. thuringiensis* complex than that on equal mass of goethite in single system, even though some sorption sites for heavy metals in individual component of oxide-bacteria composite could be occupied, masked or neutralized by their interaction (Kulczycki et al., 2005; Song et al., 2009).

Biphasic kinetics of the sorption was observed in current study. The rapid sorption was probably ascribed to the chemical reaction or film diffusion (Bunzl et al., 1976, Grossl and Sparks, 1994; Sparks et al., 1999). Interparticle or intraparticle diffusion into pores or solids was probably accounted for the slow sorption (Bruemmer et al., 1988; Barrow et al., 1989). On goethite, the initial sorption rate (h) of Cr was higher than that of Cu while the opposite behavior was observed in comparing the pseudo-second-order rate constant (k). Higher initial sorption rate of Cr than that of Cu was just in agreement with the greater affinity of Cr than that of Cu for goethite (Table 15), and might be ascribed to the higher first hydrolysis constant of Cr ($10^{-4.0}$) than Cu ($10^{-8.0}$) (Smith and Martell, 1976). The intraparticle diffusion of heavy metals could be the limited step on the sorption rate in whole sorption process and the ionic radius of the metal was generally regarded as the controlling factor in intraparticle diffusion (Bruemmer et al., 1988; Barrow et al., 1989). The ionic radius of Cu^{2+} and Cr^{3+} was 0.72 and 0.63, respectively. However, Cu^{2+} and $Cr(OH)^{2+}$ were the dominant species of Cu and Cr at pH 4.5 (Adriano, 2001; Bradl, 2004), the ionic

radius of $Cr(OH)^{2+}$ was certainly greater than that of Cr^{3+} and was probably greater than that of Cu^{2+}, thus accounted for the slower sorption rate of Cr than Cu on goethite in whole sorption process. Both initial sorption rate and sorption rate in whole sorption process of heavy metals were higher on goethite-*B. thuringiensis* complex than that on pure goethite. It was probably owing to the preferential sorption of heavy metals on the biotic fraction of bacteria-goethite complex as discussed above. Electronegativity of heavy metal has been considered as one of the factors in controlling their affinity in biosorption (Abu Al-Rub et al., 2006), faster rate of Cu than Cr on the sorption by goethite-*B. thuringiensis* complex was in line with their ESC (Table 15), and might be due to the greater electronegativity of Cu (1.90) than Cr (1.66).

Stronger competition between Cu and Cr was observed on goethite-*B. thuringiensis* complex than on goethite and the selectivity of both sorbents were greater for Cr than for Cu. Metal sorption on soil components can be either specific or non-specific (Sparks, 2002; Bradl, 2004). Specific sorption was found to be the primary mechanism of heavy metal sorption on goethite by the formation of various kinds of inner-sphere complexes (Charlet and Manceau, 1992; Peacock and Sherman, 2004). On bacteria, some studies reported that nonspecific sorption was the primary mechanism of heavy metal retention (Shuttleworth and Unz, 1993; Ledin et al., 1997; Zouboulis et al., 2004), whereas other studies demonstrated that specific sorption was the main mechanism (Boyanov et al., 2003; Burnett et al., 2006; Guiné et al., 2006). By monitoring the release of Mg^{2+}, Ca^{2+} and H^{+} during the adsorption of Cu^{2+}, Cd^{2+}, Zn^{2+} and Mn^{2+} on a fungal cell (*Saccharomyces cerevisiae*), Avery and Tobin (1993) found that covalent bonding (H^{+} displacement) of the metal was greater at low metal concentrations, while weaker electrostatic interactions (Mg^{2+} plus Ca^{2+} displacement) became increasingly important at higher metal concentrations. Similar viewpoint has been implied by Pagnanelli et al. (2003). On the other hand, the affinity of goethite-*B. thuringiensis* complex for heavy metals was lower than that of pure goethite (Table 15), Chen et al. (2009) also found that goethite contained more high-affinity binding sites for Cu than bacteria (*Pseudomonas putida* CZ1) at pH4.5 even at low metal

concentration (0.025 mmol L^{-1}). Nonspecific sorption is generally not stronger than specific sorption since the difference in reversibility between outer-sphere complex and inner-sphere complex (Antoniadis and Tsadilas, 2007). Competitive sorption among heavy metal takes place mainly on low-affinity sites (Qin et al., 2006). The reaction of heavy metal with goethite-*B. thuringiensis* complex thus was probably more reversible than that with pure goethite, and it was confirmed by the greater desorption of sorbed metals from the former sorbent than that from the latter (Table 16). The exchange of one metal by the other in competitive sorption might be unimportant on goethite since the less irreversibility of specific sorption. Preferential sorption of Cr over Cu on goethite was just in line with their behavior in initial sorption rate (Table 14). The competition between Cu and Cr on goethite thus could be due to their difference in initial sorption rate. Higher initial sorption rate of Cr gave rise to the priority in occupying the active sites. However, on goethite-*B. thuringiensis* complex, the selectivity of the sorbent was still greater for Cr than for Cu even though the initial sorption rate of Cr was slower than that of Cu, which could be due to the higher ESC of Cu than Cr (Table 15). Greater proportion of sorbed Cu was distributed on the biotic fraction of goethite-*B. thuringiensis* complex, more metals of Cu than that of Cr could be sorbed as reversible state. Therefore, iron exchange was probably the primary mechanism of competitive sorption between Cu and Cr on goethite-*B. thuringiensis* complex.

5.4 Conclusions

In this work, the competitive sorption and desorption of Cu and Cr were investigated on/from goethite and goethite-*B. thuringiensis* complex. Sorption isotherms and kinetics showed that the sorption of heavy metals was more and faster on goethite-*B. thuringiensis* complex than that on goethite and was suppressed by their competition. The competitive sorption between Cu and Cr was more intensive on goethite-*B. thuringiensis* complex than on goethite and the competitive ability of Cr was stronger than that of Cu on both sorbents. Desorption of sorbed heavy metals by $Ca(NO_3)_2$ was usually slightly higher from single systems than that from binary

systems. The lower amounts (percentages) of heavy metals desorbed from goethite than from goethite-*B. thuringiensis* complex confirmed the higher affinity of heavy metals for the former than for the latter sorbent.

6. Sorption of Cu, Pb and Cr on Na-Montmorillonite: Competition and the Effect of Macroelements

6.1 Materials and methods

6.1.1 Materials and Chemicals

Wyoming Na-montmorillonite (SWy-2) used in current study was bought from the Source Clays Repository of the Clay Minerals Society (Columbia, MO). The specific surface area determined by water adsorption (S_w) and point of zero charge (PZC) of Na-montmorillonite was 636 $m^2\ g^{-1}$ and 2.5, respectively. Deionized distilled water was used to prepare all the solutions, all the chemicals [$Cu(NO_3)_2{\cdot}3H_2O$, $Pb(NO_3)_2$, $Cr(NO_3)_3{\cdot}9H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, $Ca(NO_3)_2$, $Mg(NO_3)_2{\cdot}6H_2O$, KNO_3] used in present study were analytical grade.

6.1.2 Sorption experiments

Preliminary experiments revealed that 4 h was enough for Cu, Pb and Cr to attain the sorption equilibrium. Sorption isotherm of each heavy metal at pH 3.5, 4.5 and 5.5 was observed by mixing different amount of individual heavy metal with 50 mg of montmorillonite in 20 ml of KNO_3 (0.02 mol L^{-1}). Sorption of each heavy metal (200 mmol kg^{-1}) on 50 mg of montmorillonite was also studied at pH from 3.5 to 6.5. Competitive sorption of three heavy metals in ternary system at pH 3.5, 4.5 and 5.5 was investigated by adding equal amount (50, 100 or 200 mmol kg^{-1}) of each metal simultaneously. The sorption of constant amount (200 mmol kg^{-1}) of individual heavy metal on 50 mg of montmorillonite in 20 ml of KNO_3 (0.02 mol L^{-1}) at pH 3.5, 4.5 and 5.5 were observed in the presence of each macroelement (Al, Fe, Ca, Mg) with increasing the molar ratio of macroelement to heavy metal ($R_{m/h}$) from 0 to 15. The pH of each sample was kept constant at the desired value by 0.1 mol L^{-1} KOH or HNO_3. The samples were shaken at 20°C for 4 h. The suspensions were then centrifuged at 10,000 *g* for 20 min and filtered through a 0.22-μm membrane filter. The concentration of the heavy metal in the supernatant was determined by atomic absorption spectrometry (Perkin-Elmer A Analist 700). The amount of each heavy

metal sorbed was calculated by the difference between the quantity of heavy metal added initially and that present in the supernatant.

Sorption experiments in present study were performed in triplicate and the relative standard deviation was lower than 5%.

6.2 Results

6.2.1 Sorption isotherms of Cu, Pb and Cr at different pH

Sorption isotherms of Cu, Pb and Cr at pH 3.5, 4.5 and 5.5 on montmorillonite are depicted in Fig. 15. The data were fitted by Langmuir equation: $X = X_m KC/(1+KC)$, where C is the concentration (mmol L^{-1}) of heavy metal in equilibrium solution, X is the amount (mmol kg^{-1}) of each metal sorbed at corresponding C on montmorillonite, X_m is the maximum amount that may be sorbed (sorption capacity), and K is a constant related to the binding energy. The greater the K value, the higher the affinity of the heavy metal for montmorillonite (Sparks, 2002). The Langmuir parameters are listed in Table 17. It was observed that both sorption capacity and affinity of each heavy metal increased slightly with the increase of pH, the sorption capacity of three heavy metals followed the sequence of Cr (196.4-211.7 mmol kg^{-1}) > Pb (121.9-171.7 mmol kg^{-1}) > Cu (106.0-132.9 mmol kg^{-1}) while the order of Cr >> Cu > Pb (pH 3.5 and 4.5) and Cr >> Pb > Cu (pH 5.5) were found on their sorption affinity. Higher capacity of Cr than that of Cu and Pb was in line with the study of Abollino et al. (2003).

Table17 Isotherm parameters for the sorption of Cu, Pb and Cr on Na-montmorillonite at pH 3.5, 4.5 and 5.5

Heavy metal	pH 3.5			pH 4.5			pH 5.5		
	X_m (mmol kg^{-1})	K	R^2	X_m (mmol kg^{-1})	K	R^2	X_m (mmol kg^{-1})	K	R^2
Cu	106.0	3.51	0.97	120.2	5.46	0.99	132.9	6.21	0.95
Pb	121.9	2.45	0.98	139.0	4.84	0.98	171.7	7.87	0.98
Cr	196.4	32.66	0.97	206.7	37.09	0.95	211.7	83.37	0.91

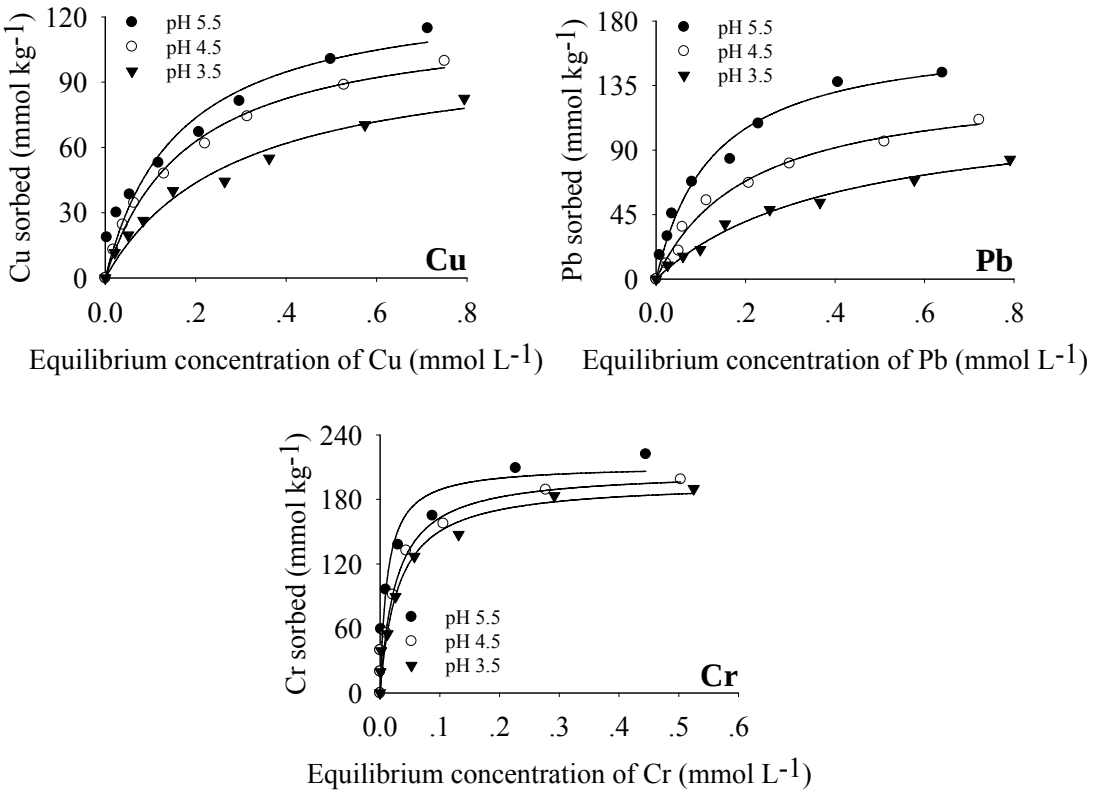

Fig.15. Langmuir sorption isotherms of Cu, Pb and Cr on Na-montmorillonite at pH 3.5, 4.5 and 5.5

6.2.2 Effect of pH on the sorption of Cu, Pb and Cr

The effect of pH on the sorption of heavy metals is displayed in Fig. 16. With the increase of pH from 3.5 to 6.5, the sorption percentage of Cu, Pb and Cr increased from 28% to 53%, 27% to 76% and 74% to 87%, respectively. The pH value at which 50% of the amount of a given heavy metal sorbed is called pH_{50}. In pH-dependent sorption, it was generally regarded that the lower the pH_{50} the higher the affinity of a metal for the sorbent (Kinniburgh et al., 1976; Violante et al., 2008). The pH_{50} value of heavy metals on montmorillonite in current study followed the sequence of Cu > Pb >> Cr, the indicated affinity sequence (Cr >> Pb > Cu) was in agreement with that revealed by sorption isotherms at pH 5.5 (Table 17).

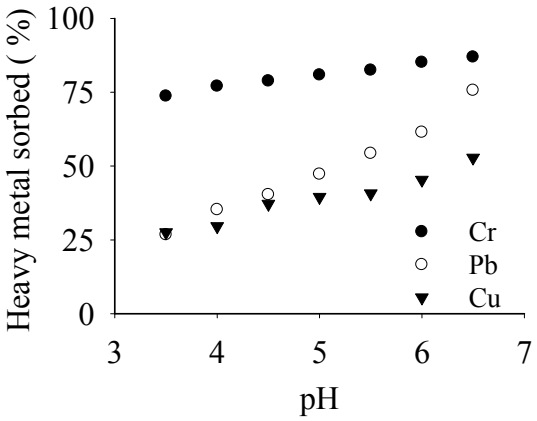

Fig.16. Effect of pH on the sorption of Cu, Pb and Cr by Na-montmorillonite

6.2.3 Competitive sorption of Cu, Pb and Cr in ternary system at different pH and surface coverage

Competitive sorption among equal amount of Cu, Pb and Cr in ternary system on montmorillonite at pH 3.5, 4.5 and 5.5 were investigated at different surface coverage. Negligible competition among heavy metals was observed at pH 5.5 (data not shown). The sorption of heavy metals in single and ternary system at pH 3.5 and 4.5 are recorded in Table 18. In order to evaluate their competition, the inhibitive efficiency of the other two heavy metals on the sorption of a selected metal was calculated according to the following expression:

Inhibitive efficiency (%) = (1- the sorption of selected heavy metal in ternary system / the sorption of selected heavy metal in single system) × 100.

For each heavy metal, the inhibitive efficiency decreased with the increase of pH. For example, when the initial addition of each heavy metal was 50 mmol kg^{-1}, the inhibitive efficiency for Cu, Pb and Cr decreased from 36%, 58% and 10% at pH 3.5 to 11%, 36% and 7% at pH 4.5. However, an increasing trend of inhibitive efficiency for each heavy metal was found with the increase of surface coverage. For instance, with increasing the initial addition of each heavy metal from 50 to 200 mmol kg^{-1}, the inhibitive efficiency for Cu, Pb and Cr increased from 36%, 58% and 10% to 68%, 93% and 26%, respectively. These results suggested that the competitive sorption among heavy metals on montmorillonite was intensified by the increase of surface

coverage while relieved by the increase of pH, negligible competition among heavy metals was observed when the pH was raised to 5.5. The greatest inhibitive efficiency for Pb and the lowest inhibitive efficiency for Cr indicated that the competitive ability of three examined heavy metals in simultaneous sorption on montmorillonite followed the sequence of Cr >> Cu > Pb in ternary system.

Table18 Competitive sorption of Cu, Pb and Cr with different concentration of initial addition in ternary system on Na-montmorillonite at pH 3.5 and 4.5

Concentration (mmol kg^{-1})	Heavy metal	pH 3.5			pH 4.5		
		Single System (mmol kg^{-1})	Ternary System (mmol kg^{-1})	*IE	Single System (mmol kg^{-1})	Ternary System (mmol kg^{-1})	*IE
50	Cu	24.7	15.8	36%	29.9	26.6	11%
	Pb	17.5	7.4	58%	28.6	18.4	36%
	Cr	46.9	42.2	10%	46.9	43.6	7%
100	Cu	40.1	16.1	60%	48.0	30.2	37%
	Pb	38.4	11.2	71%	55.0	20.8	62%
	Cr	89.6	74.4	17%	91.5	83.3	9%
200	Cu	55.0	17.6	68%	74.3	25.3	66%
	Pb	53.5	3.7	93%	80.7	9.7	88%
	Cr	147.4	109.1	26%	157.6	130.8	17%

*IE stands for the inhibitive efficiency of a selected heavy metal by the other two competing metals

6.2.4 Sorption of Cu, Pb and Cr in the presence of increasing concentrations of macroelement at different pH

Sorption percentage of Cu, Pb and Cr on montmorillonite in the presence of increasing concentrations of macroelement at pH 3.5, 4.5 and 5.5 are illustrated in Fig.

17-19. The promotive (+) or inhibitive (-) efficiency of macroelement on the sorption of heavy metal was calculated as follows to evaluate the difference among Al, Fe, Ca and Mg in affecting the sorption of Cu, Pb and Cr:

Percentage efficiency (%) = (1- the sorption of heavy metal in the presence of macroelement / the sorption of heavy metal in the absence of macroelement) × 100.

It was observed that the sorption of Cu, Pb and Cr generally decreased with the increase of Ca and Mg concentrations at pH 3.5, 4.5 and 5.5 (Fig. 17-19). The inhibitive efficiency by both Ca and Mg for examined heavy metals decreased with the increase of pH and followed the sequence of Pb > Cu >> Cr at pH 3.5 and Cu > Pb >> Cr at pH 4.5 and 5.5 (Table 19), confirming the more intensive competition at lower pH and the strongest sorption of Cr on montmorillonite.

The influence of Al and Fe concentrations showed different patterns on the sorption of Cu, Pb and Cr by montmorillonite at pH 3.5, 4.5 and 5.5 (Fig. 17-19; Table 19). The presence of Al species prevented the sorption of Cu and Pb completely within lower $R_{m/h}$ at pH 3.5, the sorption of Cr was also inhibited significantly by Al species at pH 3.5 but a fraction of Cr was still sorbed even when the $R_{m/h}$ was raised to 15. Sharp increase in inhibitive efficiency at lower $R_{m/h}$ followed by a stable trend at higher $R_{m/h}$ was found on the sorption of Cu, Pb and Cr in the presence of Al species at pH 4.5. At pH 5.5 and in the presence of Al species, the sorption of Cr was promoted markedly while the sorption of Pb was still inhibited at examined $R_{m/h}$, but the inhibitive efficiency increased at lower $R_{m/h}$ and then decreased at higher $R_{m/h}$. An inhibitive effect at lower $R_{m/h}$ followed by a promotive influence at higher $R_{m/h}$ was observed for the sorption of Cu at pH 5.5 in the presence of Al species. Diverse influences of Fe species on the sorption of examined heavy metals were also found in current study. A complete inhibition of Cu sorption by Fe species within lower $R_{m/h}$ was observed at pH 3.5, the sorption of Pb and Cr were also inhibited at examined $R_{m/h}$ at pH 3.5 but a decrease trend in inhibitive efficiency was found at higher $R_{m/h}$. Chromium was completely sorbed by the presence of Fe species within lower $R_{m/h}$ at pH 4.5, while the sorption of Cu and Pb was depressed at the same pH, but the inhibitive efficiency increased initially and decreased at higher $R_{m/h}$. At pH 5.5 and in

the presence of Fe species, the sorption of Cu was slightly depressed at lower $R_{m/h}$ and then stimulated gradually, while the sorption of Pb and Cr was facilitated gradually and significantly, respectively. These results suggested that the sorption of heavy metals on montmorillonite was depressed by Al and Fe species similar to that by Ca and Mg when the pH and / or the concentration of Al and Fe species was lower, while Al and Fe species with higher concentration promoted the sorption of heavy metals especially at higher pH. Moreover, by comparing the inhibitive and promotive efficiency, it seemed that the inhibition of macroelements on heavy metal sorption generally followed the order of Al > Fe > Ca > Mg while Fe species was more efficient than Al species in promoting the sorption of heavy metals (Fig. 17-19; Table 19).

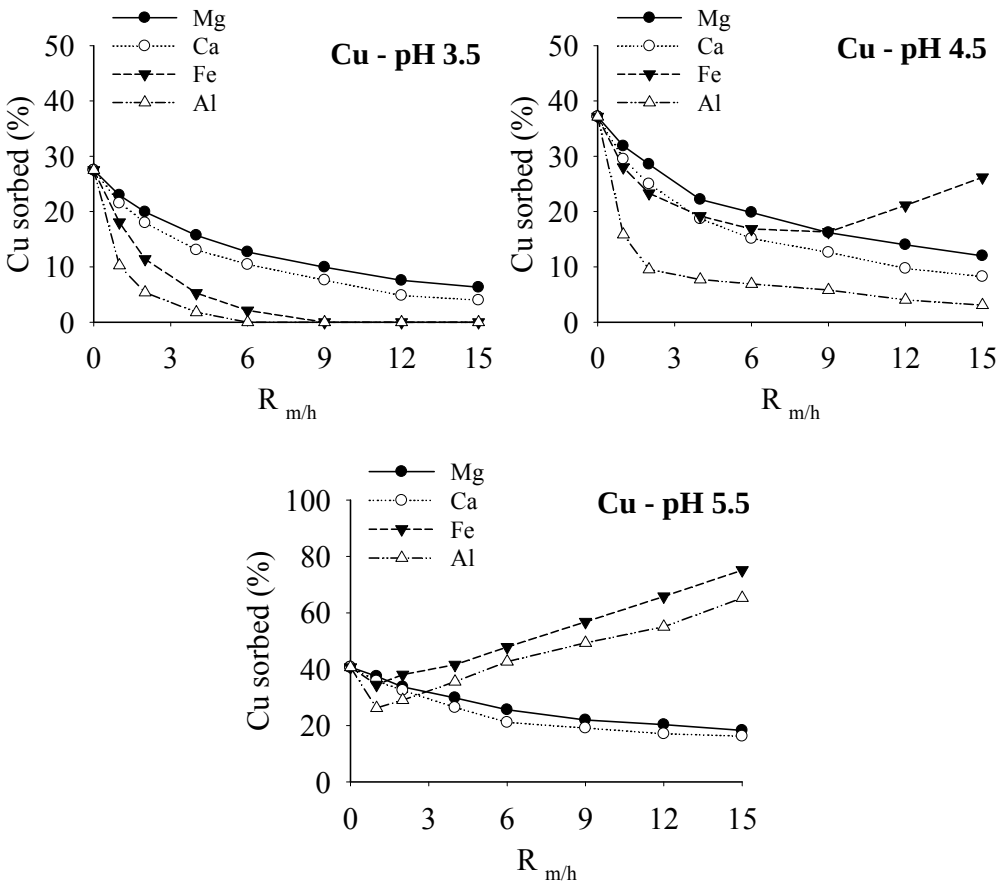

Fig.17. Effect of concentration of Al, Fe, Ca and Mg on the sorption of Cu by Na-montmorillonite at pH 3.5, 4.5 and 5.5

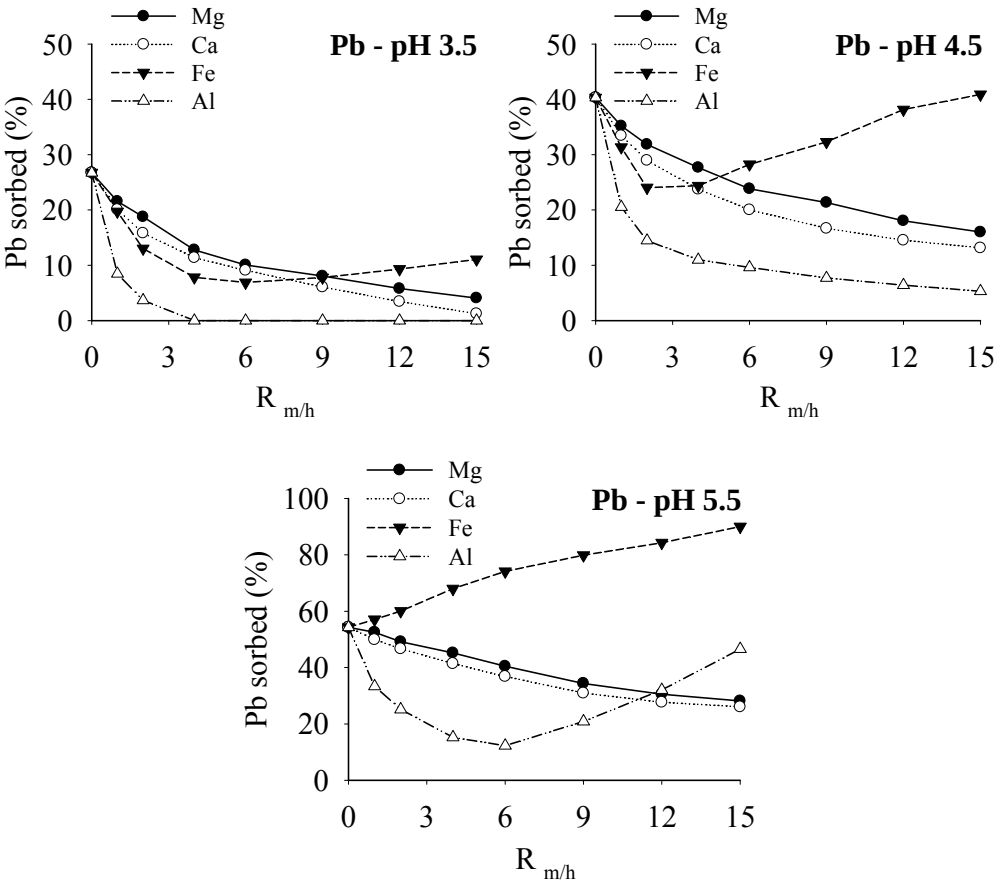

Fig.18. Effect of concentration of Al, Fe, Ca and Mg on the sorption of Pb by Na-montmorillonite at pH 3.5, 4.5 and 5.5

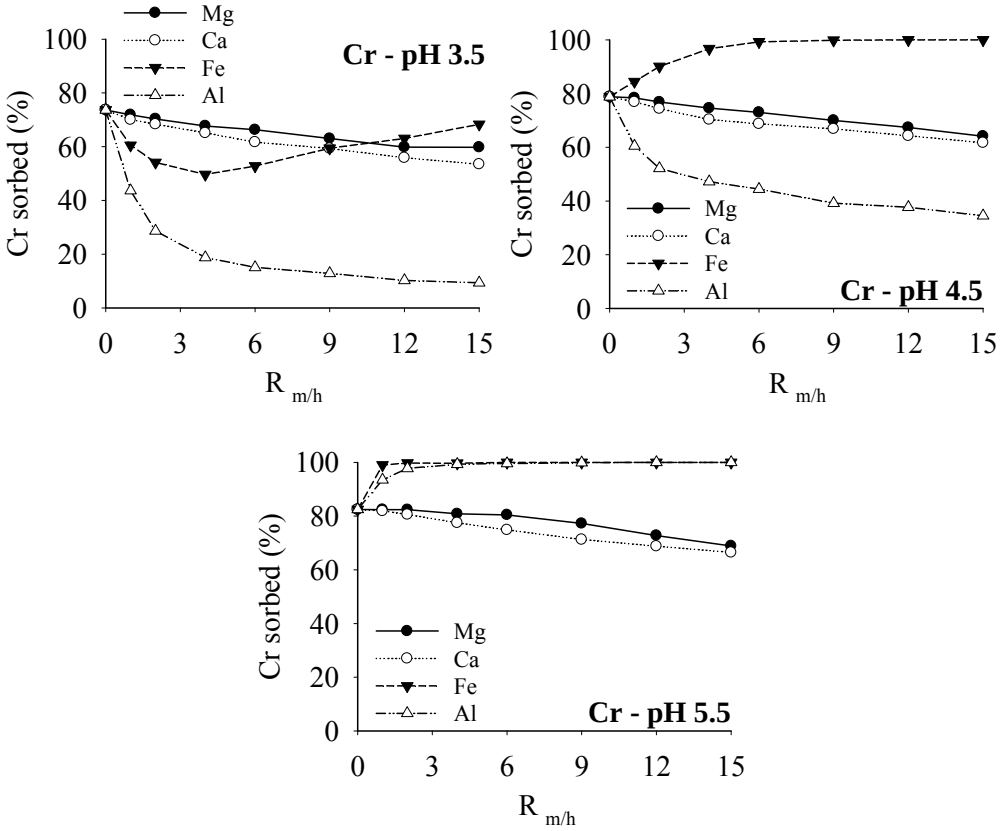

Fig.19. Effect of concentration of Al, Fe, Ca and Mg on the sorption of Cr by Na-montmorillonite at pH 3.5, 4.5 and 5.5

Table19 Promotive (+) or inhibitive (-) efficiency of Al, Fe, Ca and Mg on the sorption of Cu, Pb and Cr by Na-montmorillonite (%)

Heavy metal	R m/h	pH 3.5				pH 4.5				pH 5.5			
		Al	Fe	Ca	Mg	Al	Fe	Ca	Mg	Al	Fe	Ca	Mg
Cu	1	- 63	- 34	- 22	- 16	- 57	- 25	- 21	- 14	- 36	- 15	- 12	- 8
	2	- 80	- 59	- 35	- 28	- 74	- 37	- 33	- 23	- 29	- 6	- 20	- 17
	4	- 94	- 81	- 53	- 43	- 79	- 48	- 50	- 40	- 13	+ 2	- 35	- 27
	6	- 100	- 92	- 62	- 54	- 81	- 55	- 59	- 47	+ 5	+ 18	- 48	- 37
	9	- 100	- 100	- 72	- 64	- 84	- 56	- 66	- 56	+ 21	+ 40	- 53	- 46
	12	- 100	- 100	- 83	- 73	- 89	- 43	- 74	- 62	+ 35	+ 62	- 58	- 50
	15	- 100	- 100	- 86	- 77	- 92	- 30	- 78	- 68	+ 60	+ 85	- 60	- 55
Pb	1	- 68	- 26	- 25	- 19	- 49	- 22	- 17	- 13	- 39	+ 5	- 8	- 3
	2	- 86	- 51	- 41	- 30	- 64	- 40	- 28	- 21	- 54	+ 11	- 14	- 9
	4	- 100	- 71	- 57	- 52	- 73	- 40	- 41	- 31	- 72	+ 25	- 24	- 17
	6	- 100	- 74	- 66	- 62	- 76	- 30	- 50	- 41	- 77	+ 37	- 32	- 25
	9	- 100	- 71	- 77	- 70	- 81	- 20	- 59	- 47	- 62	+ 47	- 43	- 37
	12	- 100	- 65	- 87	- 78	- 84	- 5	- 64	- 55	- 41	+ 55	- 49	- 44
	15	- 100	- 59	- 95	- 85	- 87	+ 1	- 67	- 60	- 14	+ 66	- 52	- 48
Cr	1	- 41	- 18	- 5	- 2	- 23	+ 7	- 2	- 1	+ 13	+ 20	- 1	0
	2	- 61	- 27	- 7	- 5	- 34	+ 14	- 6	- 2	+ 19	+ 21	- 2	0
	4	- 75	- 33	- 12	- 8	- 40	+ 23	- 11	- 5	+ 20	+ 21	- 6	- 2
	6	- 80	- 28	- 16	- 10	- 44	+ 26	- 13	- 7	+ 21	----	- 9	- 2
	9	- 83	- 19	- 19	- 14	- 50	+ 27	- 15	- 11	+ 21	----	- 14	- 6
	12	- 86	- 14	- 24	- 19	- 52	----	- 18	- 14	----	----	- 17	- 12
	15	- 87	- 7	- 27	- 19	- 56	----	- 22	- 19	----	----	- 19	-16

6.3 Discussions

A selectivity sequence of Cr >> Cu > Pb in ternary sorbate system was observed on their competitive sorption by montmorillonite at pH 3.5 and 4.5. Two mechanisms have been proposed for the sorption of heavy metals on montmorillonite, the one was the sorption on the edge sites by forming inner-sphere complex similar to that on iron or aluminum oxide, while the other one was the sorption on the planar sites by forming outer-sphere complex through ion exchange reaction (Strawn and Sparks, 1999; Hyun et al., 2000; Morton et al., 2001; Undabeytia et al., 2002; Gu et al., 2010). Moreover, since the irreversibility of inner-sphere complex while the reversible nature of outer-sphere complex, it was generally considered that the sorption on the edge sites was resistant to the increase of electrolyte concentration while the sorption on the planar sites was electrolyte concentration dependent (Strawn and Sparks, 1999; Hyun et al., 2000; Morton et al., 2001). The sorption of Cu, Pb and Cr in the presence of increasing concentrations of Ca and Mg in current study could be regarded as the influence of electrolyte concentration on the sorption of heavy metals. The inhibitive efficiency of Ca and Mg on the sorption of examined heavy metals followed the sequence of Cu > Pb >> Cr at pH 4.5 and 5.5, which may suggest that the proportion of sorbed heavy metals located on the edge sites of montmorillonite followed the order of Cr >> Pb > Cu while that on the planar sites followed the opposite sequence (Cu > Pb >> Cr) at relative higher pH regions (pH 4.5 and 5.5). Furthermore, the sequence of sorption proportion of examined heavy metals on the edge sites of montmorillonite at relative higher pH regions was confirmed by the affinity sequence revealed by pH_{50} values (Fig. 16). The intrinsic natures such as first hydrolysis constant, electronegativity and softness of heavy metals are the important factors in comparing their sorption behavior on the same sorbent (Gomes et al., 2001). The distribution sequence of Cr >> Pb > Cu on the edge sites of montmorillonite was just in accordance with their first hydrolysis constant [$Cr(10^{-4.0})$ >> $Pb(10^{-7.7})$ > $Cu(10^{-8.0})$] (Smith and Martell, 1976). The consistency of sorption affinity of heavy metals with their first hydrolysis constant has also been found on hydroxyaluminum-montmorillonite complexes (Saha et al., 2002). According to

Walker et al. (1988), the formation of outer-sphere complex was the dominated mechanism for the sorption of Al^{3+} on montmorillonite at pH range between 3.0 and 4.1, the complete inhibition of Al^{3+} on the sorption of Cu and Pb by montmorillonite at pH 3.5 in current study probably indicate that the sorption of both heavy metals in this pH was governed by nonspecific sorption. Furthermore, the inhibitive sequence of Pb > Cu >> Cr by Ca and Mg was observed at pH 3.5 (Table 19), which may suggest that the affinity of interlayer sites for Cu was greater than that for Pb. Our results was in agreement with Gu et al. (2010) that the affinity of Pb for variable charge sites on montmorillonite was greater than that of Cu, but was different from Gu et al. (2010) in affinity sequence of Pb and Cu on permanent charge sites, probably due to the difference in microstructure of montmorillonite or the concentration of heavy metals applied. Actually, Abollino et al. (2003) pointed out that the introduction of Pb and Cd into the interlayer of Na-montmorillonite was less available than that of other divalent heavy metals including Cu since the larger ionic radius [Pb(1.20) > Cu(0.72)], which resulted in greater steric hindrance. Therefore, Cr had more homogeneous sorption sites with Pb than that with Cu on montmorillonite, less competence of Pb than Cr in competition for edge sites and than Cu in competition for interlayer sites resulted in the weakest selectivity in ternary system.

The sorption of Cu, Pb and Cr on montmorillonite was generally inhibited by Ca and Mg, while Al and Fe showed different patterns of influence including inhibition and promotion on the sorption of heavy metals, depending on the solution pH and macroelement concentration. The inhibition of macroelements on the sorption of Cu, Pb and Cr by montmorillonite was certainly due to their competition with examined heavy metals for homogeneous sorption sites as discussed above. Greater depression by Al and Fe than that by Ca and Mg at lower pH was owing to the higher charge density of trivalent metals. Stronger inhibition by Ca than that by Mg was in accord with the higher affinity of the former cation than the latter for montmorillonite as observed by Sposito et al. (1983). Diverse influence of Al and Fe in affecting heavy metal sorption was ascribed to their complicated behavior in aqueous media. It is well known that Al^{3+} and Fe^{3+} can not only act as counterions to compress the electrical

double layers around negatively charged clays, but also form various hydroxylated species by hydrolysis and polymerization when their concentration and / or solution pH is relative higher (Mcbride and Bloom, 1977; Ma and Pierre, 1999; Liu et al., 2005). The promotive effect of Al or Fe on the sorption of heavy metals by montmorillonite at higher pH and / or greater concentration of macroelements in present study was probably related to the hydrolysis and polymerization of Al^{3+} and Fe^{3+} on clay mineral, which may result in the formation of hydroxyl-Al- or hydroxyl-Fe-intercalated montmorillonite or amorphous-Al- or amorphous-Fe-(hydr)oxide coated montmorillonite (Carstea, 1968; Oades, 1984; Guand and Doner, 1990; Ma and Pierre, 1999). Greater sorptions of heavy metals by hydroxyl-Al-intercalated montmorillonite compared to that by untreated montmorillonite at relative higher pH have been reported by several previous studies (Harsh and Doner, 1984; Lothenbach et al., 1997; Saha et al., 2001, 2002; Janssen et al., 2007). Green-Pedersen and Pind (2000) also found that ferrihydrite coated montmorillonite showed higher sorption capacity for Ni than equal mass of pure montmorillonite. Greater capacity and higher affinity of Al or Fe polymers or (hydr)oxides than the fraction of montmorillonite in their complexes for the sorption of heavy metals have also been found by the above studies (Lothenbach et al., 1997; Green-Pedersen and Pind, 2000; Saha et al., 2001, 2002; Janssen et al., 2007), the similar advantage and preference was probably the driven force for the promotion of Fe and Al species on the sorption of heavy metals in current study. Greater promotion by Fe species than that by Al species in present study was probably due to the higher hydrolysis constant of Fe^{3+} than Al^{3+} (Smith and Martell, 1976), the hydrolysis and polymerization of Fe^{3+} thus was more easily occurred than that of Al^{3+} with the same concentration or at the same pH (Stumm and Morgan, 1996). Therefore, the competition between macroelement and heavy metal was the explanation for the inhibition on heavy metal sorption while the hydrolysis or polymerization of Fe^{3+} and Al^{3+} on clay mineral and the following formation of hydroxyl-Fe- or hydroxyl-Al-montmorillonite or amorphous-Fe- or amorphous-Al-(hydr)oxide coated montmorillonite probably accounted for the promotion on the sorption of heavy

metals.

It was noteworthy that Al species promoted the sorption of Cu in most range of examined $R_{m/h}$ while inhibited the sorption of Pb at all examined $R_{m/h}$ range at pH 5.5. However, the visible inhibition on the sorption of Cu at lower ratio of $R_{m/h}$ while the durative promotion on the sorption of Pb at all examined $R_{m/h}$ range by Fe species was observed at the same pH (Fig. 17, 18; Table 19). This different influence of Al and Fe species on the sorption of Cu and Pb may be related at least in part to the fact that Al precipitates showed higher affinity for Cu than for Pb while Pb had stronger affinity than Cu for Fe precipitates as reported by Kinniburgh et al. (1976) and Potter and Yong (1999).

6.4 Conclusions

The selectivity of montmorillonite for Cu, Pb and Cr followed the sequence of Cr >> Cu > Pb in simultaneous sorption, the competition among heavy metals was relieved by the increase of pH and intensified by the increase of surface coverage. The sorption of heavy metals on montmorillonite was generally inhibited by Ca and Mg, while Al and Fe could inhibit or promote the sorption of heavy metal, depending on the solution pH and the concentration of macroelements. The sequence of Al > Fe > Ca > Mg was observed in the inhibition of macroelements on heavy metal sorption while higher efficiency of Fe species over Al species was found in their promotion on the sorption of heavy metals. These results are of vital importance for evaluating the mobility of heavy metals in natural environment.

7. Sorption/Desorption of Arsenate on/from Mg-Al Layered Double Hydroxides: Influence of Phosphate

7.1 Materials and methods

7.1.1 Synthesis of Mg-Al-Cl-LDH

The layered double hydroxide (hydrotalcite) of Mg-Al type, containing chloride (LDH-Cl) was prepared by the coprecipitation method described by Costantino and Pinnavaia (1995). A solution containing $MgCl_2$ $6H_2O$ and $AlCl_3$ $6H_2O$ (initial Mg/Al molar ratio of 2) was slowly added with stirring at 20°C to a NaOH solution at pH 10.0. The suspension was kept at this pH by adding 2 mol L^{-1} NaOH. No effort was made to minimize contact with the atmospheric air during the preparation of the LDHs, in order to simplify the preparation method. The final suspension was aged 20 h at 20°C, centrifuged at 10,000 g for 30 min, washed five times with deionized water and then dialyzed, freeze dried and lightly ground to pass through a 0.315 mm sieve. Subsamples of this material were also preheated in a oven for 2 h at 150, 250, 350 or 450°C. The precipitates obtained at 20°C (LDH-Cl-20) or preheated at 450°C (LDH-Cl-450) were used for sorption studies.

7.1.2 Synthesis of Mg-Al-CO_3-LDH

The layered double hydroxide containing carbonate (LDH-CO_3) was prepared by the coprecipitation method described by Ulibarri et al. (2001), slowly adding a stoichiometric mixture of $Mg(NO_3)_2$ H_2O and $Al(NO_3)_3$ H_2O (initial Mg/Al molar ratio of 2) to a vigourously stirred solution containing NaOH (3.4 mol L^{-1}) and Na_2CO_3 (1 mol L^{-1}). The final pH was 13. As previously described the suspension was aged 20 h at 20°C, centrifuged, washed with deionized water and then dialyzed, freeze dried and lightly ground to pass through a 0.315 mm sieve. Subsamples of this material were also preheated in a oven for two h at 150, 300 or 450°C. The precipitates obtained at 20°C (LDH-CO_3-20) or preheated at 450°C (LDH-CO_3-450) were used for sorption studies.

The minerals were characterized by X-ray diffraction (XRD) and FT-IR analyses.

The X-ray diffraction patterns of randomly oriented samples were obtained using a Rigaku diffractometer (Rigaku Co., Tokyo) equipped with Cu Kα radiation generated at 40 kV and 30 mA and a scan speed of 2° 2θ min^{-1}. The XRD traces were the results of eight summed signals. The FT-IR spectra of the samples were obtained using a Perkin-Elmer Spectrum One FT-IR Spectrophotometer (Perkin Elmer USA).

The surface area of the samples was determined by H_2O sorption at 20% relative humidity according to the method of Quirk (1955).

7.1.3 Sorption experiments

Suitable amounts of 0.01 mol L^{-1} solutions containing KH_2AsO_4 or KH_2PO_4 were added to 100 mg of the uncalcined and calcined LDH minerals, previously equilibrated at pH 6.0, in order to have initial arsenate or phosphate concentration in the range 5×10^{-5} to 7.5×10^{-3} mol L^{-1}. The pH of each suspension was kept constant for 24 h by adding 0.1 or 0.01 mol L^{-1} HCl or NaOH. Experiments of arsenate sorption onto the four materials were carried out also at different pH values (pH from 4.0 to 11.0) by adding suitable amounts of arsenate (a quantity 40% higher than that necessary to reach a maximum sorption at pH 6.0 as determined by sorption isotherm).

The final suspensions (20 ml) were centrifuged at 10,000 g for 20 min and filtered through a 0.22-µm membrane filter. Arsenate or phosphate in the final solutions was determined by ion chromatography, using a Dionex DX-300 Ion Chromatograph (Dionex Co, Sunnyvale, CA) (Pigna et al., 2006). The phosphate standard concentration was 0.1 to 2 mmol L^{-1}, the arsenate standard concentration was 0.05 to 0.5 mmol L^{-1}. The amount of arsenate or phosphate sorbed was determined by the difference between the initial and final concentrations.

7.1.4 Competitive sorption of arsenate and phosphate

One hundred mg of LDH-Cl-20 or LDH-Cl-450 were equilibrated at 20°C in reaction flasks at pH 4.5, 6.0 and 9.0. Suitable amounts of 0.01 mol L^{-1} solutions containing equimolar amounts of arsenate and phosphate were added as a mixture in

order to have 500 or 1000 mmol of arsenate and phosphate per kg of sample. The suspensions, whose pH was kept constant by adding 0.1 or 0.01 mol L^{-1} HCl or NaOH, were kept to react from 0.5 to 168 h. Some experiments were carried out by adding arsenate or phosphate 3 h before the other oxyanion (*AsO_4 before PO_4* or *PO_4 before AsO_4* systems). The suspensions were kept to react for further 24 h by keeping the pH constant. The final suspensions (20 ml) were centrifuged at 10,000 g for 20 min and filtered through a 0.22-µm membrane filter. Arsenate or phosphate in the final solutions were determined as previously described

7.1.5 Kinetics of desorption of arsenate

Suitable amounts of arsenate were added to water suspensions containing 100 mg of each sample in order to have a final surface coverage of arsenate of about 70% (as determined by sorption isotherms) and kept to react for 24 h at pH 6.0. Previous experiments demonstrated that all arsenate added was completely sorbed onto the LDHs. A large amount of phosphate (phosphate/arsenate molar ratio 3) was then added to the suspensions to have a phosphate concentration in solution sufficiently high to facilitate arsenate desorption (Pigna et al., 2006). The suspensions were allowed to react from 0.16 to 400 h. Arsenate and phosphate was determined in the supernatants by ion chromatography, as discussed before.

7.2 Results and discussions

7.2.1 Nature of the LDHs

The X-ray diffraction patterns of LDH-Cl showed sharp and symmetrical peaks at 0.775, 0.388, 0.259, 0.152 and 0.149 nm and some asymmetric peaks at high angles (> 30° 2Θ) (Fig. 20 Aa), characteristic of hydrotalcite (Miyata, 1975; Cavani et al., 1991; Costantino and Pinnavaia, 1995; Ulibarri et al., 2001; Rives, 2002). Basal spacing calculated from the 003 reflection was 0.769 Å for LDH-CO_3 (not shown). XRD diffraction patterns of both the minerals heated at 150 or 250°C did not show significant change with temperature (not shown). After heating at 450°C the materials showed the disappearance of the peaks of hydrotalcite, due to the distruction of the

structure of these minerals (Fig. 20 Ab) and the appearance of broad peaks at about 0.255, 0.210 and 0.150 nm attributable to the formation of Mg-Al mixed oxides (Hibino et al., 1995; Socías-Viciana et al., 2008).

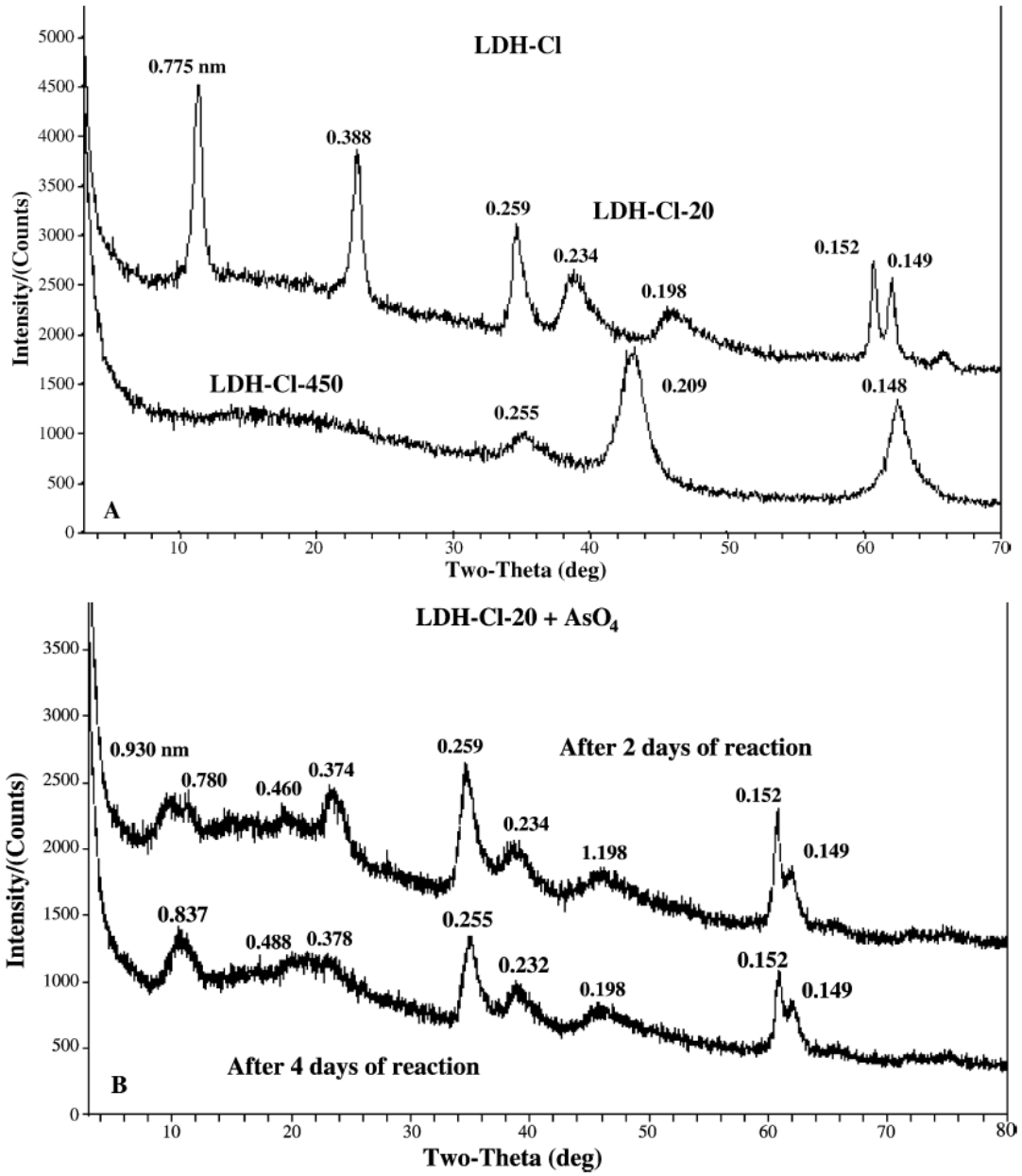

Fig.20. Powder X-ray diffraction patterns of LDH-Cl (A) and LDH-Cl after addition of arsenate at pH 6.0 (1400 mmol kg^{-1}) after 2 days or 4 days of reaction (B)

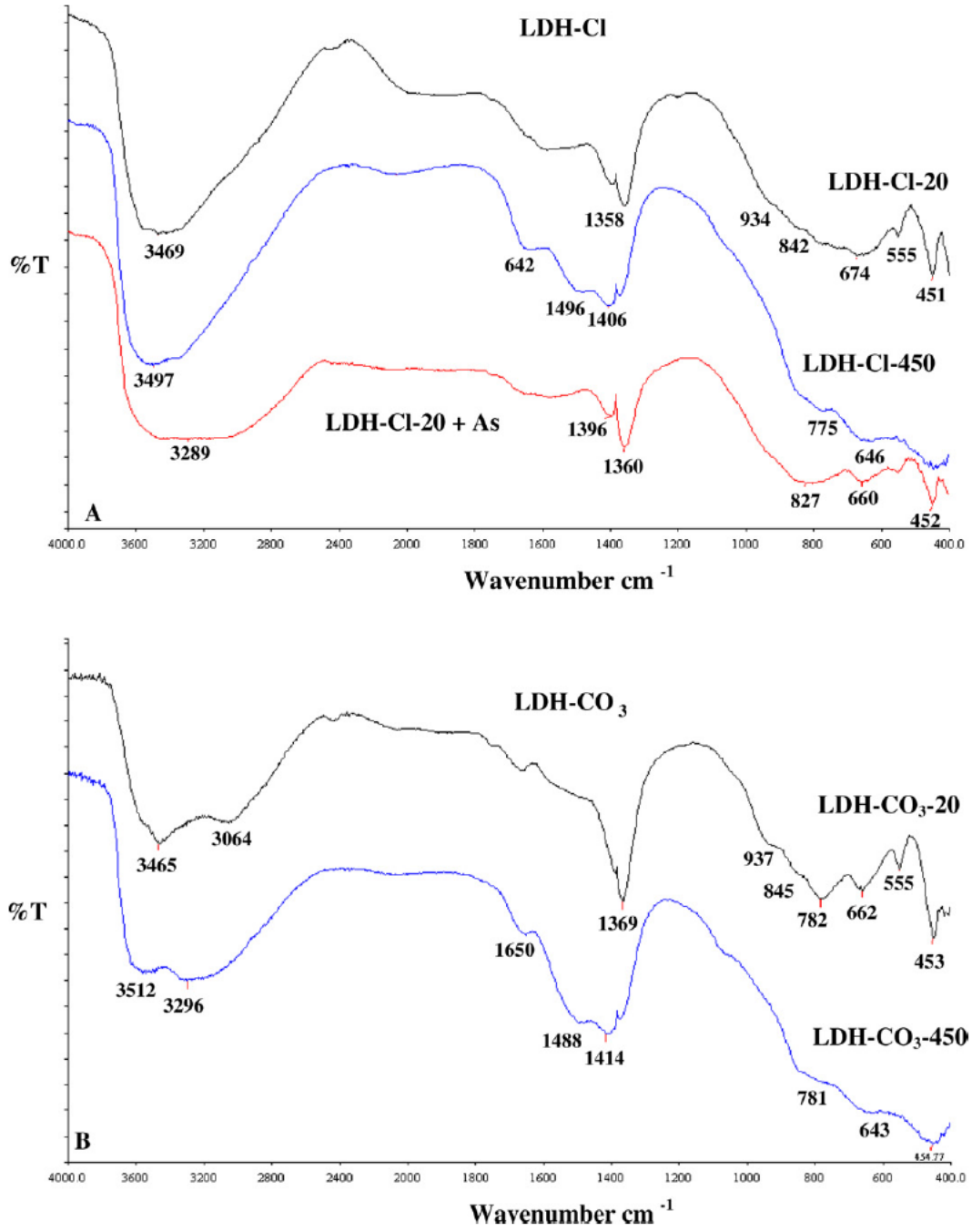

Fig.21. FTIR spectra of LDH-Cl (A) and LDH-CO_3 (B) minerals

The FT-IR spectra of LDH-Cl and LDH-CO_3 are shown in Fig. 21. Both the spectra showed a peak in the hydroxyl stretching region centered at about 3465-3500 cm^{-1}, attributed to the hydroxyls attached to Al and Mg and peaks at about 950, 780, 555 cm^{-1} which can be ascribed to Al-O stretching modes. A shoulder at about 3060 cm^{-1}, interpreted as an interaction between the OH groups and the interlayer carbonate ions (Rives, 2002; Lv et al., 2006) and the peaks at about 1370, 865 and 665 cm^{-1},

assigned to interlayer carbonate, were particularly strong in LDH-CO_3 (Fig. 21 Ba), whereas were absent or much more reduced in LDH-Cl (Fig. 21 Aa), indicating that carbonate was present only as an impurity in the latter sample. The FT-IR spectra of the materials preheated at 450°C showed a strong decrease in intensity of the peak at about 1370 cm^{-1} (mainly in LDH-CO_3-450), which was accompanied by the appearance of new peaks at about 1500 and/or 1415 cm^{-1} attributed to carbonate species (Yang et al., 2005). FT-IR analyses evidenced that carbonate was not completely removed after heating at 450°C and strengthen the findings of Hibino et al. (1995) who demonstrated that when a LDH-CO_3 mineral with an initial Al/Mg molar ratio of 0.33 was heated to 500°C, 20-30% of the carbonates still remained in the material.

The sample LDH-Cl-20 showed a surface area (421 m^2 g^{-1}) much greater than that of the sample LDH-CO_3-20 (225 m^2 g^{-1}) (Table 20). After heating at 450°C the surface area of LDH-Cl slightly decreased to 395 m^2 g^{-1}, whereas the surface area of LDH-CO_3 tremendously increased to 515 m^2 g^{-1}. Such an increase of the surface area of the latter mineral must be attributed to the removal of CO_2 and water after heating which promotes the formation of channels and then creates a material particularly porous and reactive (as discussed below) (Cavani et al., 1991; Hibino et al., 1995; Ulibarri et al., 2001; Lv et al., 2006).

7.2.2 Sorption of arsenate and phosphate onto LDHs

The isotherms of sorption at pH 6.0 of arsenate and phosphate added alone onto LDH-Cl and LDH-CO_3 formed at 20°C or preheated at 450°C are shown in Fig. 22. The sorption data of arsenate or phosphate sorbed onto the minerals conformed to the Langmuir equation in the following form: $X = X_m KC/(1+KC)$, where X is the amount of arsenate or phosphate sorbed per unit mass of adsorbent (mmol kg^{-1}), X_m is the maximum amount of arsenate or phosphate that may be bound to the adsorbent (sorption capacity), C is the equilibrium solution concentration (mmol L^{-1}), and K is a constant related to the binding energy (Sparks, 2002).

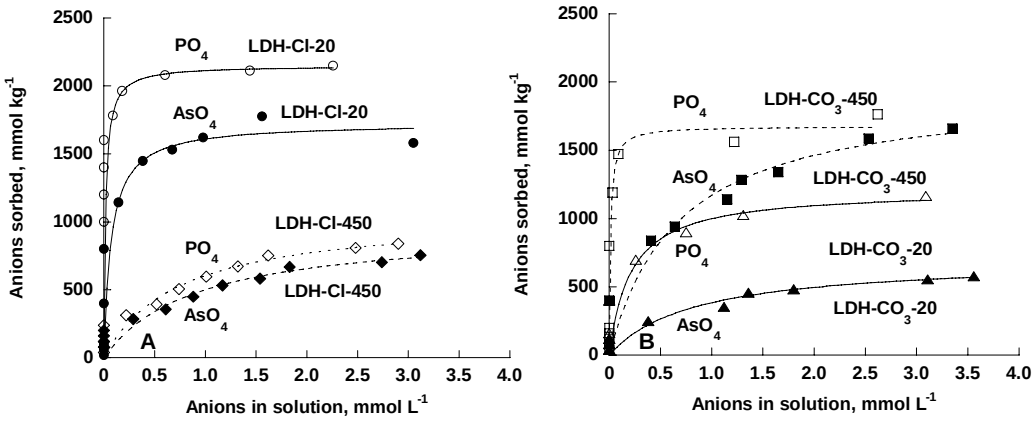

Fig.22. Sorption isotherms at pH 6.0 and 20 °C of arsenate (AsO_4) and phosphate (PO_4) onto uncalcined (LDH-Cl-20 (A) and LDH-CO_3-20 (B)) and calcined (LDH-Cl-450 (A) and LDH-CO_3-450 (B)) minerals

The shape of the isotherms of phosphate sorbed on LDHCl-20 and LDH-CO_3-20 and arsenate sorbed on LDH-Cl-20 indicates a high affinity behavior, the sorption being characterized by a rapid rise at low phosphate or arsenate equilibrium concentration. Vice versa, the sorption of both the two oxyanions on LDH-Cl-450 and LDH-CO_3-20 and of arsenate on LDH-CO_3-450 increased slowly when the ligand equilibrium concentration increased, due to a weaker affinity for the anions for these sorbents. This trend is confirmed analyzing the values of the Langmuir constant K (Table 20).

The uncalcined and calcined samples LDH-Cl and LDH-CO_3 showed a different behaviour in fixing the two oxyanions. More phosphate than arsenate was sorbed onto the minerals but whereas LDH-Cl-450 sorbed much lower amounts of both the ligands than LDH-Cl-20 (Fig. 22A), vice versa, LDH-CO_3-450 showed a capacity to sorb arsenate and phosphate much greater than LDH-CO_3-20 (Fig. 22B; Table 20). The reduction in sorption of the oxyanions on LDH-Cl-450 compared to their sorption on LDH-Cl-20 cannot be ascribed to the negligible reduction in surface area of this material (a decrease of less than 4%; Table 20), but to the formation of mixed Mg-Al oxides after heating which reduced the capacity of this sample to sorb arsenate and phosphate. On LDH-CO_3-20 the high affinity of carbonate anions for LDH layers strongly prevented arsenate or phosphate sorption (Ulibarri et al., 2001). After heating

at 450°C large amounts of carbonate anions were lost facilitating the sorption of arsenate and phosphate onto the porous and particularly reactive material which formed.

After addition of 1400 mmol arsenate per kg onto LDH-Cl-20 at pH 6.0 and a reaction time of 2 or 5 days at 20 °C the XRD pattern of the mineral showed small and broad peaks centered at about 0.930, 0.840, 0.785, 0.600 and/or 0.460 nm (Fig. 20 B). These findings indicated that arsenate was included with time into the layer space of this anionic clay. Vice versa, the XRD pattern of LDH-CO_3-20 remained practically unchanged after arsenate addition (not shown), indicating that arsenate was not able to remove carbonate ions from the interlayers (Ulibarri et al., 2001).

The effect of pH (4.0-11.0) on the sorption of arsenate onto the uncalcinated and calcinated samples after 24 h of reaction is shown in Figure 23. Arsenate sorption decreased by increasing pH on all the sorbents. This behavior must be attributed to the high affinity of OH^- for LDHs (Miyata, 1975; You et al., 2001) and/or to the value of zero point charge (pzc) of the sorbents. The PZC for uncalcined LDHs was reported to be in the range 7.0-9.0 (Kim et al., 2005), so in alkaline systems the sorption of arsenate anions onto the LDH surfaces should be inhibited.

Table 20 Surface area, maximum sorption capacity (S_m) for arsenate (AsO_4) and phosphate (PO_4), K and R^2 as obtained from the sorption isotherms of LDH samples

Sample	Surface area	AsO_4			PO_4		
	(m^2 g^{-1})	X_m (mmol kg^{-1})	K	R^2	X_m (mmol kg^{-1})	K	R^2
LDH-Cl-20	421.2 ± 12	1727	13.8	1.00	2150	55.5	1.00
LDH-CO_3-20	225.0 ± 8	701	1.2	0.92	1209	4.74	0.92
LDH-Cl-450	395.1 ± 6	954	1.1	0.96	1053	1.35	0.95
LDH-CO_3-450	514.8 ± 14	1992	1.3	0.92	1676	80.9	096

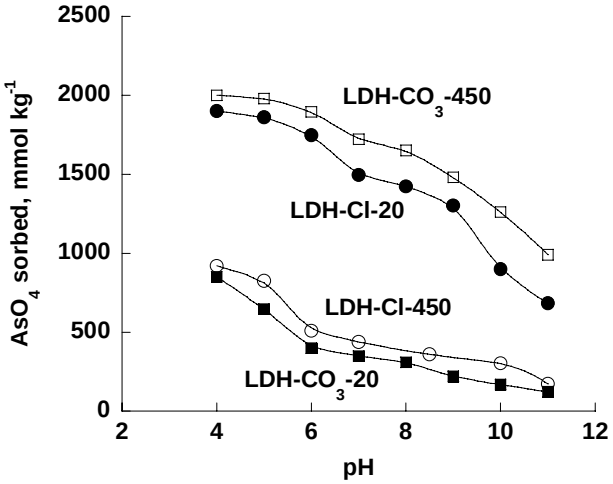

Fig.23. Effect of pH on the sorption of arsenate (AsO_4) on uncalcined (LDH-Cl-20 and LDH-CO_3-20) and calcined (LDH-Cl-450 and LDH-CO_3-450) minerals

7.2.3 Competitive sorption of arsenate and phosphate

Competition in sorption between arsenate and phosphate as affected by reaction time on the uncalcined and calcined LDH minerals was studied at pH 6.0 (Table 21) by adding the ligands as a mixture (AsO_4+PO_4) at an initial arsenate/phosphate molar ratio of 1. The quantities of both the oxyanions added (1000 mmol of arsenate and 1000 mmol of phosphate per kg of LDH-Cl-20 and 500 mmol of arsenate and 500 mmol of phosphate per kg of LDH-CO_3-20) corresponded to a surface coverage of phosphate near 50 or 25 %, respectively. More phosphate than arsenate was sorbed on the sorbents during the reaction period, but the final arsenate sorbed/phosphate sorbed molar ratio (rf) increased with time and reached a value near to 1 even after 168 h of reaction or more. However, it is interesting to note that when phosphate was added alone on the sorbents (2000 or 1000 mmol of phosphate per kg of LDH-Cl-20 or LDH-CO_3-20, respectively) it was completely sorbed within few hour, whereas equal amounts of arsenate and phosphate added as a mixture were not completely sorbed even after 168 h, evidently for the competition in sorption of these ligands, characterized by different size, on the surfaces of the LDH minerals.

The rf values, particularly during the first 24 h, were greater for LDH-Cl-20 than for LDH-CO_3-20, indicating a greater affinity of phosphate for the latter than for the former sorbent (Table 21). Furthermore, we have found that the calcinated samples

showed rf values much lower than those ascertained for the uncalcined samples (Table 21). For example, in the first 5 h of reaction rf ranged from 0.24 to 0.73 for LDH-CO_3-450 and from 0.10 to 0.44 for LDH-Cl-450 (data not shown).

Table 21 Effect of reaction time on the amounts of arsenate (AsO_4) and phosphate (PO_4) sorbed on LDH-Cl-20 and LDH-CO_3-20; 1000 and 500 mmol kg^{-1} of each oxyanions were added to LDH-Cl and LDH-CO_3, respectively.

Sample	Time (h)	AsO_4 sorbed	PO_4 sorbed	rf	AsO_4 + PO_4	PO_4 added alone (2000 mmol kg^{-1})
		mmol kg^{-1}			mmol kg^{-1}	
LDH-Cl-20	0.5	431	772	0.56	1203	1366
	1	561	870	0.64	1431	1617
	3	636	903	0.70	1539	1888
	5	815	950	0.86	1765	1969
	16	836	968	0.86	1804	2000
	24	872	973	0.89	1845	2000
	48	874	970	0.90	1844	2000
	168	878	989	0.89	1867	2000
	Time (h)	AsO_4 sorbed	PO_4 sorbed	rf	AsO_4 + PO_4	PO_4 added alone (2000 mmol kg^{-1})
		mmol kg^{-1}			mmol kg^{-1}	
LDH-CO_3-20	0.5	198	404	0.49	602	721
	1	241	438	0.55	679	814
	3	279	472	0.59	751	855
	5	314	478	0.65	792	888
	16	359	490	0.73	849	922
	24	434	495	0.88	929	957
	48	446	500	0.89	946	1000
	168	458	500	0.92	958	1000

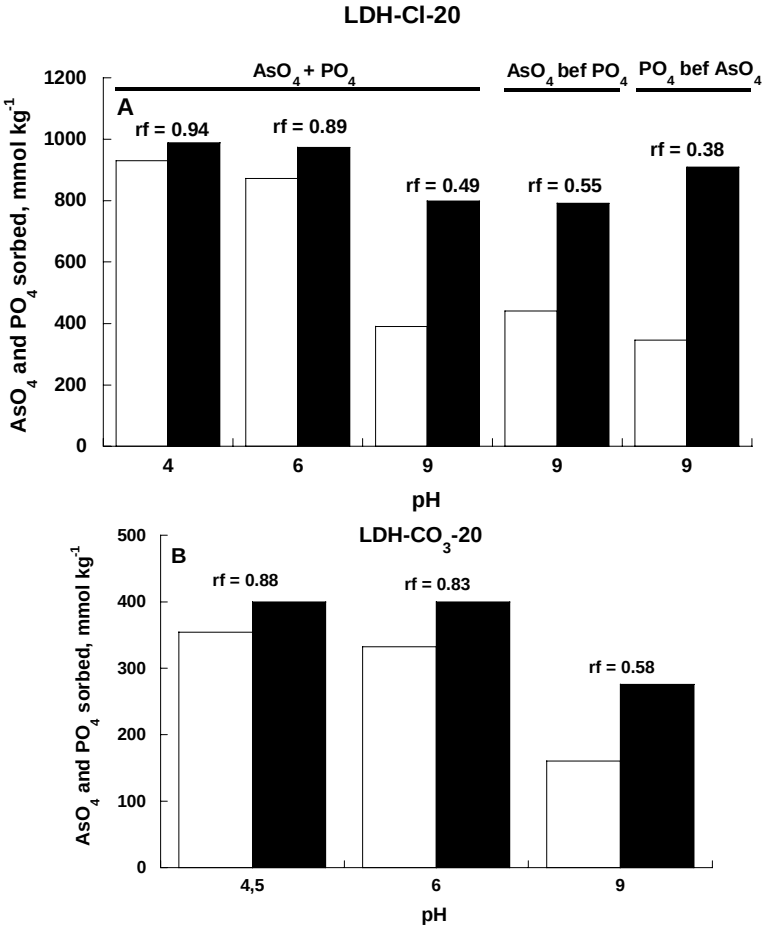

Fig.24. Amounts of arsenate (AsO_4) and phosphate (PO_4) sorbed on LDH-Cl-20 (A) and LDH-CO_3-20 (B) at pH 4.5, 6.0 and 9.0 when the two oxyanions were added as a mixture (AsO_4 + PO_4) or by adding AsO_4 3 h before PO4 (AsO_4 bef PO_4) or vice versa (PO_4 bef AsO_4). rf stands for AsO_4 sorbed/PO_4 sorbed molar ratio

Competition in sorption between arsenate and phosphate was also affected by pH and sequence of the anions addition. In Fig. 24A are reported the amounts of the oxyanions sorbed on LDH-Cl-20 (Fig. 24A) and LDH-CO_3-20 (Fig 24B) when the two ligands were added as a mixture at different pH values (4.5, 6.0 and 9.0). After 24 h of reaction the rf values were always lower than 1, but decreased by increasing pH. At pH 9.0, the amounts of the ligands sorbed strongly decreased and the rf values were particularly low, indicating that in alkaline systems OH^- ions competed with both phosphate and arsenate (as discussed before), but clearly they inhibited arsenate much more than phosphate sorption. We have also found that by adding arsenate or phosphate 3 h before the other ligand (*AsO_4 before PO_4 or PO_4 before AsO_4*), the rf

values after further 24 h of reaction at pH 9.0 increased or decreased, respectively, as compared with the rf values found in AsO_4+PO_4 systems (Fig. 24A).

7.2.4 Desorption of arsenate by phosphate from DHLs

We also studied the effect of the reaction time on the desorption of arsenate previously sorbed onto the LDH minerals by phosphate (phosphate/arsenate molar ratio of 3; Figure 25). Suitable amounts of arsenate were previously added to each mineral in order to have a final surface coverage of 70% (Table 20 and Fig. 22) and kept to react for 24 hours for complete sorption before phosphate addition. The amounts of arsenate removed from the minerals increased with time, but its desorption was characterized by an initial very fast removal followed by a much slower desorption. The kinetic of reaction desorption was well described by an Elovich equation (Fig. 25B and 25D). The kinetics of desorption of the metalloid from LDH-Cl (Fig. 25A) during the reaction period of 016 to 400 h was linear, whereas showed a "break" from LDH-CO_3 (Fig. 25D), probably indicating removal of arsenate from surface sites of different affinity (Pigna et al., 2006).

The percentage of arsenate desorbed by phosphate was higher from the uncalcined than calcined samples. In fact, more than 80% of arsenate initially sorbed was replaced after 400 h from LDH-CO_3-20, whereas only 35% were desorbed from LDH-CO_3-450 (Fig. 25D). Evidently, after heating at 450 °C mixed Mg-Al oxides formed and facilitated the sorption of arsenate forming strong inner-sphere complexes. The removal of arsenate from variable charge minerals has been demonstrated to be particularly difficult (Pigna et al., 2006; Violante et al., 2006; 2007; 2009).

In previous works some of us have studied the desorption of arsenate added to soil samples, noncrystalline or crystalline metal oxides or coprecipitated with metal [Al, Fe(III) or Fe(III)-Al] oxides (Pigna et al., 2006; Violante et al., 2006; 2007; 2009). The percentages of the metalloid desorbed by phosphate were low ranging from 2 to 30%. The initial pH, the residence time and surface coverage strongly affected the removal of arsenate from the variable charge samples. The experiments described in this work show evidence that usually larger amounts of arsenate were sorbed onto

uncalcined LDHs than on variable charge minerals (metal oxides) or soils but most of the arsenate fixed onto LDH may be removed. These findings may have important environmental implications, particularly for the removal of arsenate from polluted waters.

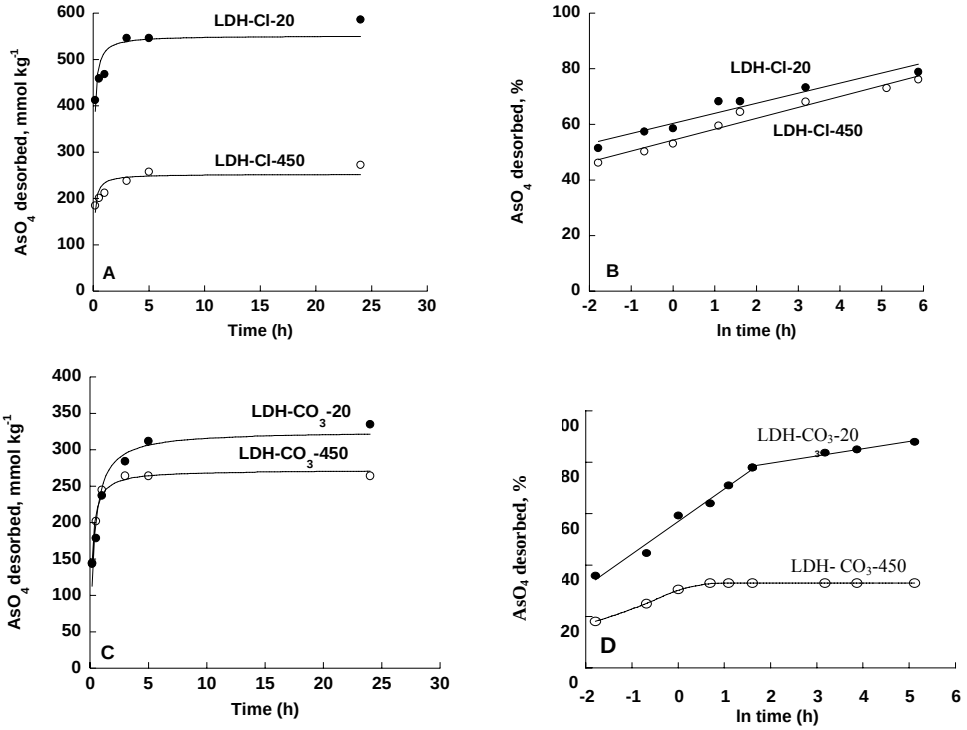

Fig.25. Kinetics of desorption of arsenate (AsO_4) by phosphate (PO_4) on LDH-Cl-20 and LDH-Cl-450 (A and C) and on LDH-CO_3-20 and LDH-CO_3-450 (B and D). In (C) and (D) the kinetics of desorption are described according to Elovich model.

7.3 Conclusions

The LDH samples (LDH-Cl and LDH-CO_3) sorbed more phosphate than arsenate, but after calcination LDH-CO_3 showed a greater capacity to sorb both the oxyanions. Competition in sorption between phosphate and arsenate was affected by pH, reaction time, surface coverage and sequence of addition of the anions. The final arsenate sorbed/phosphate sorbed molar ratio (rf) increased with reaction time or by adding arsenate before phosphate, but decreased by increasing pH and by adding phosphate before arsenate. High percentages of arsenate initially held on LDH minerals were desorbed by phosphate (about 80%), but from LDH-CO_3-450 (<40%),

probably due to the formation of strong inner-sphere complexes onto the surfaces of mixed Al-Mg oxides formed after calcination.

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